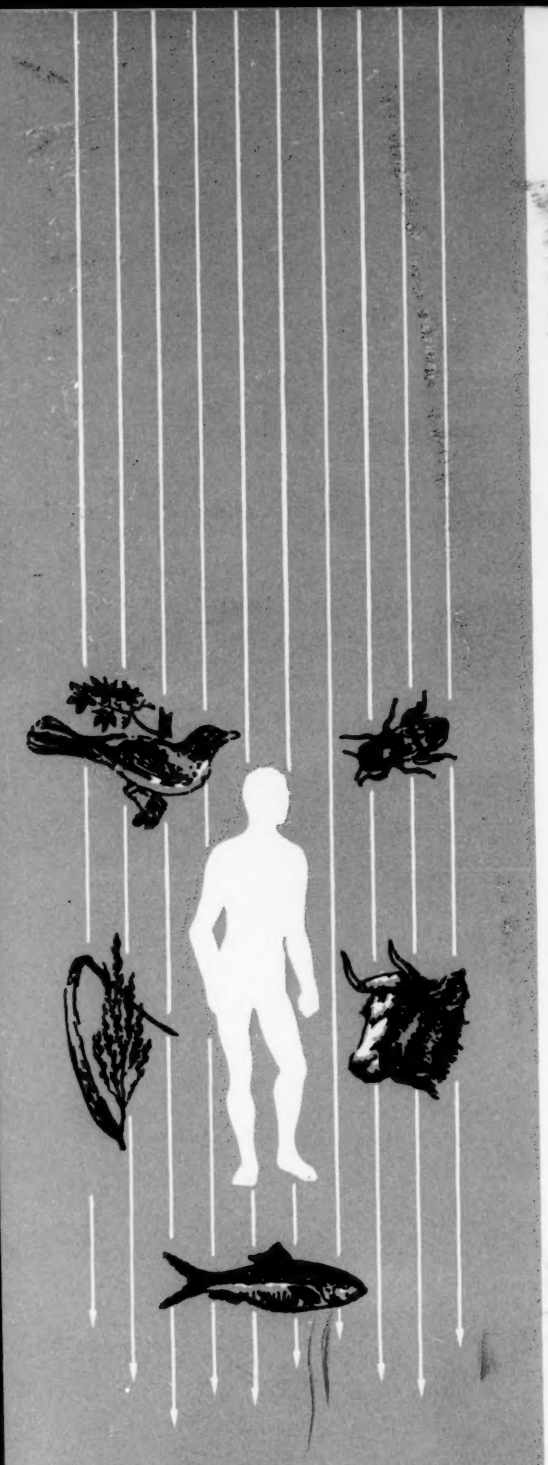

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The Working Group is comprised of representatives of the U.S. Departments of Agriculture; Commerce; Defense; the Interior; Health, Education, and Welfare; State; Transportation; and Labor; and the Environmental Protection Agency.

The Monitoring Panel consists of representatives of the Agricultural Research Service, Animal and Plant Health Inspection Service, Extension Service, Forest Service, Department of Defense, Fish and Wildlife Service, Geological Survey, Food and Drug Administration, Environmental Protection Agency, National Marine Fisheries Service, National Science Foundation, and Tennessee Valley Authority.

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SOILS

DDT Residues in Forest Floors and Soils of Western Oregon, September–November 1966

Duane G. Moore and Bobby R. Loper [1]

ABSTRACT

Between 1945 and 1965, 1.82 million hectares, or about 17 percent of the total commercial forestland in Oregon, were treated with 2.02 million kg DDT. Detectable residues of this insecticide might be present in forest soils, even those which have never received a direct application of insecticide. Forest floor and mineral soil samples were collected along four east-west transects across the Coast and Cascade Ranges. DDT residues were found in all samples, even though all but one site had never received a direct application of insecticide. In the Coast Ranges, mean concentrations of ΣDDT in forest floor samples were 0.049 ppm at the coast and 0.047, 0.064, 0.075, and 0.119 ppm at 16, 32, 48, and 64 km inland, respectively. Mean residue levels in the surface layers of mineral soil were much lower, 0.009 ppm and 0.006 ppm in the 0 to 7.5-cm and 7.5 to 15-cm depths, respectively.

Sampling sites along the Cascade Range transects were selected on the basis of elevation except that the eastern site of each transect was located 16 km east of the crest of the Cascades. Residue concentrations in forest floor samples were three to four times higher than in the Coast Ranges, but were still below 0.50 ppm. In general, ΣDDT levels increased with increasing elevation up to 1,372 meters and then decreased quite sharply east of the crest. Variations can be explained on the basis of total rainfall distribution and by transect location relative to agricultural and metropolitan centers.

Introduction

Intensified forest management is essential to meeting the ever-increasing demands for forage, recreation, timber, water, and of wildlife on our forested lands. The intensified use of our forest resources necessitated increased use of pesticides in insect, disease, and brush control programs. As a direct result, synthetic organic pesticides have become a chemical fact of life in forest protection and cultural practices.

Many pesticides in current use are rapidly detoxified in the forest environment. DDT, however, is highly resistant to degradation and may persist for extended periods of time. DDT is not currently registered by the U.S. Environmental Protection Agency (EPA) for use in forestry, but it has an extensive history of use and may be proposed to control specific pest outbreaks in the future. The present study was conducted to determine the levels and distribution of DDT residues in the forest floors and soils of western Oregon.

DDT was first applied to Oregon forests in 1945 to control an outbreak of the western hemlock looper in a 931-hectare (ha) aerial spray project near Cannon Beach (Fig. 1). Between 1945 and 1965, 1.82 million hectares, about 17 percent of the total commercial forestland in Oregon, were treated with 2.02 million kg DDT in various spray projects (Table 1). Applications were heaviest between 1949 and 1958 when 1.77 million hectares were treated in various spruce budworm spray projects.

Since 1958, about 104,682 ha have been treated with DDT, the latest project being carried out on 64,822 ha during 1974 under a Section 18 specific exemption from registration requirement granted to the Forest Service, U.S. Department of Agriculture, by the EPA.

DDT enters the forest floor and soil from direct application, drift of spray materials, rain washing through treated canopy, and litterfall, or in precipitation or dust deposited in unsprayed areas. Information on the extent of actual and potential environmental contami-

[1] Forest Service, U.S. Department of Agriculture, Forestry Sciences Laboratory, 3200 Jefferson Way, Corvallis, Oreg. 97331. The use of trade, firm, or corporation names in this publication is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the U.S. Department of Agriculture of any product or service to the exclusion of others that may be suitable.

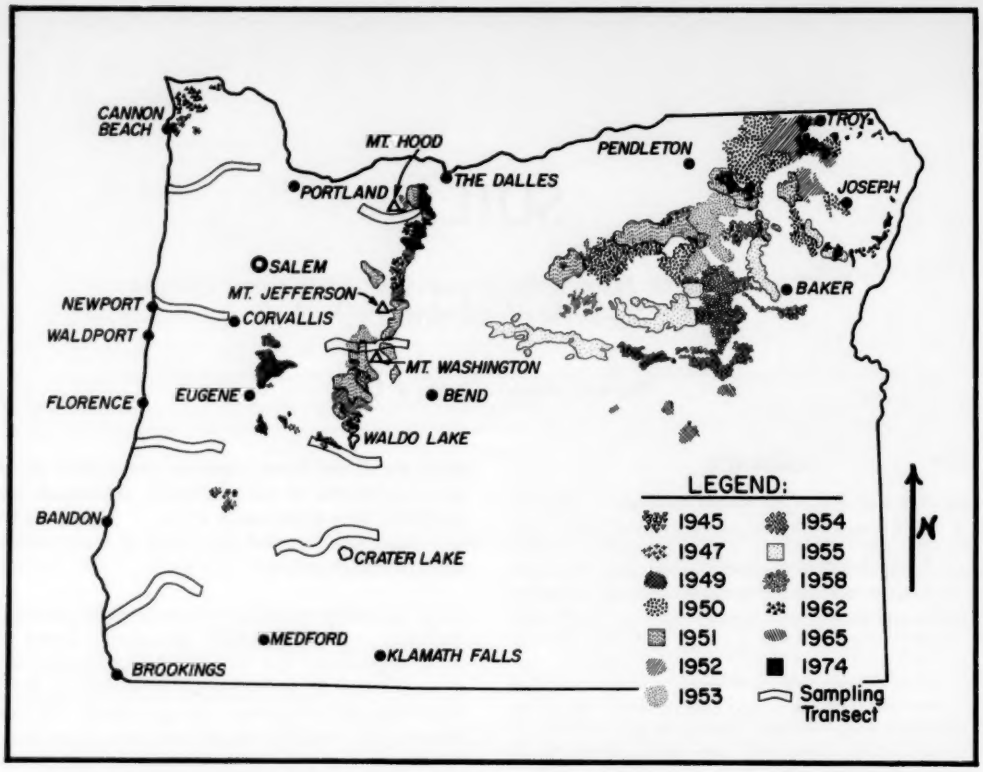

FIGURE 1. *Forest insect aerial spray projects in Oregon, and location of sampling transects*

TABLE 1. *Application of DDT to forests in Oregon, 1945–74*

Year	Hectares	DDT Applied, kg	
		By Year	Cumulative
1945	931	1,043	1,043
1947	5,666	6,350	7,393
1948	1,700	1,905	9,298
1949	109,508	122,742	132,040
1950	367,213	411,590	543,630
1951	319,986	358,656	902,286
1952	211,206	236,730	1,139,016
1953	149,815	167,920	1,306,936
1954	27,397	30,708	1,337,644
1955	251,270	281,636	1,619,280
1958	331,034	371,038	1,990,318
1962	13,152	7,371	1,997,689
1965	26,710	22,453	2,020,142
1974	64,822	54,492	2,074,634
TOTALS	1,880,410	2,074,634	

nation with pesticide residues in the forest is limited. Only a few studies have been concerned with ΣDDT. From a study conducted in a forest in New Brunswick, Canada, Woodwell (*26*) concluded that DDT residues would persist for a maximum of 10 years and that *o,p'*-DDT was leached into the subsoil. The forest had been sprayed with a total of 4.48 kg/ha of DDT between 1952 and 1958. Woodwell and Martin (*27*) reported that DDT residues in soils of heavily sprayed forests in Maine and New Brunswick had increased over a period of three years after the last application. They hypothesized that DDT residues persisted in the forest canopy and were carried to the soil by rain and litterfall.

A study in the same locality refuted Woodwell's suggestion that DDT residues were subject to differential weathering and preferential retention of *o,p'*-DDT (*28*). Yule reported that about 16 percent of the DDT originally applied still remained in surface soils after almost 20 years, and that the main component of the residue was *p,p'*-DDT. He also demonstrated that these DDT residues were unavailable to soil insects in toxic amounts (*28*).

The only environmental change reported from a study in northern Pennsylvania was a significant accumulation of DDT in the forest floor and surface soil (*6*). One year after aerial spraying at a rate of 0.56 kg/ha, no measurable increase in DDT residues was noted in fish, crayfish, or stream sediments. Belyea (*5*) measured DDT residues in soil and a related food chain in

northern Maine forests and concluded that the residues would disappear in 10–12 years. Riekerk and Gessel (*18*) reported that regardless of application rate, less than 1 percent of the DDT applied to the surface of a gravelly soil beneath a stand of Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco) leached through the surface soil over an 18-month period during which 100 cm of rainfall was recorded.

Tarrant et al. (*23*) conducted a long-term study of the behavior and fate of DDT in a forest environment in eastern Oregon after a 1965 aerial spray project. DDT residues were measured in throughfall precipitation, fresh litterfall, the forest floor and mineral soil, and in water samples from two streams draining the sprayed area. They reported that DDT residues in the forest floor had decreased by more than 50 percent after three years and had not leached into the mineral soil. Movement of DDT from the forest canopy to the forest floor was small and decreased with time. ΣDDT content of stream samples was only 0.3 ppb at the time of spraying, and this low concentration decreased rapidly to levels below the limit of detection. Only about one third of the applied chemical, however, was accounted for; 26 percent reached the forest floor initially, and another 6 percent reached the forest floor in litterfall over a three-year period. Their study did not measure the amount of DDT that had reached the forest canopy, and the extent of chemical loss from drift during spraying could not be assessed. It was assumed that a significant amount of chemical was lost to the atmosphere as drift during application or by volatilization from the canopy after spraying.

Other studies have reported the loss of significant amounts of insecticide to the atmosphere (*8, 11*). Acree et al. (*2*) demonstrated that there is significant codistillation of DDT with water at 25° to 35°C. Middleton (*15*) reported DDT residues as high as 1.71 g/1,000 cu. meters in the air adjacent to application sites. Two studies on the presence of organochlorine pesticides in rainwater were conducted in England, one in an agricultural area (*24*) and the other in London (*1*). Both studies reported detectable levels of *p,p'*-DDT and *p,p'*-DDE. Antommaria et al. (*3*) reported minimum concentrations of up to 1.14 μg/1,000 cu. meters for *p,p'*-DDT associated with suspended particulate matter in Pittsburgh, Pennsylvania, while Tabor (*22*) reported higher minimum concentrations of airborne DDT, up to 23 μg/1,000 cu. meters, mean of 4 μg/1,000 cu. meters, in agricultural communities.

Substantial use of DDT in the past, and research on deposition, persistence, and leaching characteristics of DDT, indicate that significant amounts of the insecticide may be present in the atmosphere. Rainfall and deposition of dust could result in detectable residue levels in forest soils, even those which have never received a direct application of DDT.

Sampling, Locations and Methods

The general areas sampled were the heavily forested sections of western Oregon. Sampling transects were selected in two subregions, the Coast and the Cascade Ranges. Four east-west transects were sampled in each subregion to cover western Oregon from north to south. In the Coast Ranges, sampling sites were located 0, 16, 32, 48, and 64 km inland along each east-west transect. Elevation was used to locate sampling sites in the Cascade Range. Sampling sites were located at 457, 762, 1,067, and 1,372 meters above sea level along each east-west transect across the Cascades. Sampling sites at the highest elevation, 1,372 meters, were approximately at the crest of the Cascades, and a fifth site on each transect was located 16 km east of the crest. This sampling site is in the rain shadow of the Cascade Range on each transect. Precipitation tends to decrease approximately 25 mm each 1.6 km eastward of the crest.

At each sampling site along the eight transects, four sublocations were sampled north, east, south, and west at 10, 20, 15, and 5 meters, respectively, of an arbitrarily located central point. At each point, the forest floor over a 0.4-sq. meter area was carefully removed, and approximately 1-kg samples of mineral soil were collected at each of two depths, 0 to 7.5 cm and 7.5 to 15 cm. Soil samples were collected by digging shallow soil pits and sampling horizontally into a freshly cleaned vertical face at the desired depth using a square-tipped, flat spade.

Extreme care was taken to avoid contaminating the lower sample with material from above, and all tools were cleaned between samples with acetone. Forest floor samples were placed in new, 10-kg heavyweight Kraft bags, and soil samples were placed in standard soil sample bags. All samples were stored during the day in portable cooler chests and frozen the same day they were collected. In all, 160 sublocations were sampled along the eight transects, resulting in a total of 160 forest floor samples and 320 soil samples. Sampling was accomplished over a three-month period, September–November 1966.

Analytical Procedures

Soil samples were air-dried, ground to pass a 10-mesh sieve, mixed, and subsampled. Forest floor samples were essentially dry when collected, having been collected at the end of the dry season; those containing some moisture were air-dried. All were processed carefully by hand to remove stones, and were then ground in a large Wiley mill. The ground samples were mixed and subsampled for analysis. After being ground and

mixed, the samples were held at 0°F until they could be subsampled and analyzed.

EXTRACTION

Soils—A 100-g subsample was extracted with hexane–acetone (41+59 azeotropic) in a Soxhlet extractor for 16 hr (*16*).

Forest Floor—A 25-g subsample was extracted with acetone in a Soxhlet extractor for 16 hr.

CLEANUP

The soil and forest floor extracts were transferred to individual separatory funnels and water was added to form a water–acetone (2+1) solution. The pesticides were partitioned into hexane by shaking with three 100-ml aliquots of hexane (*10*).

The hexane extracts were dried with anhydrous sodium sulfate, evaporated to 5–10 ml, and transferred to a 15-g Florisil column (*25*). The pesticides were eluted from the column with 100 ml dichloromethane–hexane (1+3). Dichloromethane was removed by evaporation, and samples were transferred with hexane to volumetric flasks for analysis.

ANALYSIS

The concentrations of DDE, *o,p'*-DDT, TDE, and *p,p'*-DDT were quantified in a MicroTek 2000 MF gas chromatograph with a 130-mc tritium electron-capture detector. This system gave good individual peak resolution at the following retention times: DDE, 5.2 minutes; *o,p'*-DDT, 6.8 minutes; TDE, 8.0 minutes; and *p,p'*-DDT, 9.5 minutes. Other instrument parameters and operating conditions were:

Column:	Pyrex, 180 cm × 2 mm ID, packed with 5 percent QF-1 (first 126 cm) and 5 percent DC-11 (last 54 cm) on 60–80-mesh Gas Chrom Q, preconditioned for 48 hr at 220°C	
Temperatures:	column	185°C
	detector	190°C
	injector	205°C
Carrier gas:	Nitrogen flowing at 30 ml/minute	

Minimum residue levels for quantitative determinations were 0.001 ppm for soil and 0.01 ppm for forest floor. Average percent recovery and range for DDT isomers and metabolites were as follows:

Form of DDT	% Recovery (Range)	
	Soil	Forest Floor
DDE	99 (92–103)	97 (93–100)
o,p'-DDT	82 (71–99)	99 (96–100)
TDE	82 (78–91)	85 (80–84)
p,p'-DDT	97 (92–100)	94 (90–97)

CONFIRMATION

Some industrial pollutants are similar to DDT in structure and properties and can interfere with its detection or identification (*12, 14, 17, 19, 20*); naturally occurring plant or soil substances may also cause analytical errors (*9, 13*). To confirm apparent DDT residues in the present study, about half the samples were analyzed by gas-liquid chromatography (GLC) with a chloride-specific, microcoulometric detection system. This step confirmed that substances with the same retention time as the DDT standards detected by the electron-capture detector did contain chlorine, but did not rule out the possible misinterpretation of polychlorinated biphenyls (PCBs) as DDT isomers and metabolites. Therefore, all samples analyzed with the microcoulometric detector were hydrolyzed with alcoholic potassium hydroxide which would chemically alter DDT and TDE, but not PCBs (*10*). Hydrolyzed samples were then re-analyzed by both electron-capture and microcoulometric detection systems. TDE, *o,p'*-DDT, and *p,p'*-DDT peaks disappeared after hydrolysis, indicating that PCBs were not present in detectable quantities and that the quantitative measurement of DDT isomers and metabolites by the electron-capture detection system was correct.

Mass spectrophotometry is the most positive means of identifying pesticides in biological samples, but in the present study, only the forest floor samples and a few of the soil samples contained sufficient DDT to allow use of this technique. Ten forest floor and two soil samples were extracted and purified for analysis. The DDT isomers and metabolites were separated by chromatography of the final hexane extract on 500-μm silica gel H thin-layer plates developed with benzene–hexane (4+96). DDT standards were co-chromatographed on both edges of the 20 × 20 cm plates. After development, a 15-cm strip in the middle of the plate was covered, and the DDT standards were located by spraying the edge of the plate with 0.5 percent silver nitrate and exposing the plate to ultraviolet light for 15 minutes. The *o,p'*-DDT, *p,p'*-DDT, and *p,p'*-DDE were scraped from the appropriate section of the center of the plate, extracted from the silica gel with hexane, and analyzed by electron-capture gas chromatography. The pesticides separated by the thin-layer method had the same retention times as the standards.

Extracts containing the individual pesticides were introduced into a Varian MAT Model CH 7 mass spectrometer with a direct inlet probe. The mass spectra for *o,p'*-DDT, *p,p'*-DDT, and *p,p'*-DDE isolated from the forest floor samples agreed with spectra of appropriate standards and with published spectra (*21*). A comparison of sample spectra with published PCB spectra (*4*) showed that no PCBs were present in the isolated pesticides. All confirmation steps gave positive evidence that the isolated and measured substances were indeed

DDT isomers and metabolites and that PCBs were not present in detectable quantities.

Results and Discussion

COAST RANGE TRANSECTS

DDT residues were found in all samples, even though all but one site had never received a direct application of insecticide. Mean concentrations of ΣDDT residues in the forest floor were 0.049 ppm at the coast and 0.047, 0.064, 0.075, and 0.119 ppm at 16, 32, 48, and 64 km inland, respectively, over all four transects (Table 2). These DDT residue levels were quite low and tended to increase progressively from the Oregon coast inland across the coastal mountain range to the western edge of cultivated inland valleys. The two northern transects terminate in forested areas adjacent to the Willamette Valley. No major insect control projects have been conducted in the coastal mountain areas of western Oregon, and the only source of DDT which could have produced these residues appears to be aerial drift from agricultural applications and municipal spray programs for control of mosquitoes and other insect pests.

TABLE 2. *ΣDDT residues in forest floors and soils of Coast Range transects of western Oregon, September–November 1966*

Transect	Sample Depth, cm	Residues, ppm[1] Distance from Coast, km 0	16	32	48	64	Transect Means
Wilson River	Forest floor	0.052	0.056	0.058	0.058	0.132	0.071
	Soil: 0–7.5	0.005	0.005	0.006	0.009	0.024	0.010
	Soil: 7.5–15	0.006	0.011	0.013	0.003	0.006	0.008
Yaquina	Forest floor	0.037	0.038	0.081	0.098	0.116	0.074
	Soil: 0–7.5	0.007	0.013	0.006	0.009	0.009	0.009
	Soil: 7.5–15	0.006	0.005	0.005	0.004	0.005	0.005
Umpqua	Forest floor	0.054	0.046	0.060	0.054	0.130	0.069
	Soil: 0–7.5	0.006	0.006	0.008	0.008	0.013	0.008
	Soil: 7.5–15	0.004	0.004	0.005	0.007	0.008	0.005
Rogue	Forest floor	0.054	0.049	0.058	0.093	0.098	0.070
	Soil: 0–7.5	0.004	0.011	0.007	0.007	0.012	0.008
	Soil: 7.5–15	0.005	0.006	0.005	0.006	0.010	0.006
Site means	Forest floor	0.049	0.047	0.064	0.075	0.119	0.071
	Soil: 0–7.5	0.005	0.009	0.007	0.008	0.015	0.009
	Soil: 7.5–15	0.005	0.006	0.007	0.005	0.007	0.006

NOTE: ΣDDT residues include *p,p'*-DDE, *o,p'*-DDT, TDE, and *p,p'*-DDT. TDE could not be quantified in all samples.
[1] Each value represents the mean total residue for four samples from that site on the transect.

Contamination of the forested areas is surprisingly uniform along the four transects, the highest residue levels occurring adjacent to areas of agricultural activity and population centers in the inland valleys and then decreasing toward the coast with greater distance from the source. Mean annual precipitation varies from 114 cm to 265 cm between the sampling points, but there is no apparent correlation between residue levels and amount of precipitation ($r = 0.16$). Even the lowest amount of precipitation was apparently adequate to bring down any aerially transported residues to the forest floor.

Residue levels of ΣDDT in samples of the surface layers of mineral soil were much lower than levels found in forest floor samples, with average concentrations of 0.009 ppm and 0.006 ppm in the 0 to 7.5- and 7.5 to 15-cm depths, respectively. Residue levels in the mineral soil showed similar but less pronounced trends in distribution compared to those observed in the forest floor. Residues reaching the forest floor were not readily leached into the mineral soil. More than 80 percent of the ΣDDT residues reaching each site remained in the forest floor.

CASCADE RANGE TRANSECTS

Residue levels of ΣDDT in the forest floor and soils at sampling sites along the east-west transects across the Cascade Range in western Oregon appear in Table 3. These sites were selected on the basis of elevation except that for the eastern site on each transect, a location 16 km east of the crest of the passes through the Cascades was selected in order to determine whether the rain shadow had any measurable effect on the level of DDT residues in the forest environment. Residue concentrations in the forest floor were three to five times higher than those found in the Coast Ranges, but were still below 0.50 ppm. Trends in residue distribution patterns are not very distinct, but in general, total residues levels increased with increasing precipitation ($r = 0.67$) and decreased quite sharply east of the crest.

TABLE 3. *ΣDDT residues in forest floors and soils of Cascade Range transects of western Oregon, September–November, 1966*

Transect	Sample Depth, cm	Residues, ppm[1] Elevation above Sea Level, Meters 457	762	1067	1372	16 km East[2]	Transect Means
Mt. Hood	Forest floor	0.344	0.433	0.326	0.417	0.271	0.358
	Soil: 0–7.5	0.010	0.009	0.010	0.011	0.013	0.011
	Soil: 7.5–15	0.006	0.007	0.005	0.006	0.010	0.007
Santiam Pass	Forest floor	0.330	0.268	0.391	1.405[3]	0.147	0.508
	Soil: 0–7.5	0.022	0.010	0.013	0.081	0.011	0.027
	Soil: 7.5–15	0.012	0.005	0.006	0.008	0.006	0.007
Willamette Pass	Forest floor	0.383	0.425	0.298	0.225	0.059	0.278
	Soil: 0–7.5	0.010	0.047	0.018	0.005	0.005	0.017
	Soil: 7.5–15	0.007	0.010	0.008	0.004	0.003	0.006
Crater Lake	Forest floor	0.111	0.110	0.138	0.192	0.105	0.131
	Soil: 0–7.5	0.013	0.012	0.007	0.007	0.008	0.009
	Soil: 7.5–15	0.005	0.007	0.004	0.005	0.006	0.006
Site means	Forest floor	0.292	0.309	0.288	0.560	0.145	0.319
	Soil: 0–7.5	0.014	0.020	0.012	0.026	0.009	0.016
	Soil: 7.5–15	0.007	0.007	0.006	0.006	0.006	0.006

[1] Each value represents the mean of four samples at that site.
[2] Eastern sampling point was located 16 km east of the crest of the Cascades.
[3] This sampling site by chance fell in an old spray unit treated in 1953.

Residue levels in the forest floor samples from the Cascade Range varied considerably between sampling sites along each transect, and even between sublocations at each site. This variation can be attributed largely to old spray projects which took place along the crest of the Cascades from Mt. Hood on the north to Waldo Lake on the south (Fig. 1). Only one sampling site was located in an area that had been sprayed with DDT, but several others were close to an old spray project or were at locations that may have received drift from more than one spray application. Spray projects were conducted along the crest of the Cascades every year from 1949 through 1953, and 1.16 million hectares were treated with a total of 1.30 million kg DDT. None of the treated areas was included in more than one control project, but adjacent units were sprayed in consecutive years. The sampling site at 1,372-meter elevation on the Santiam Pass transect was sprayed in 1953, and 13 years later the forest floor at this site still contained an average concentration of 1.405 ppm ΣDDT. The low mean annual temperature at this high-elevation site would greatly reduce the rate of normal degradation.

Levels of ΣDDT residues in the surface of 7.5-cm layer of mineral soil are almost double the concentration found at the same depth in the Coast Range samples, but the mean concentrations at the 7.5–15-cm depth are identical. The resistance of DDT residues in the forest floor against downward transport by leaching, even at mean annual precipitation levels of 305 cm, is markedly evident in these data.

Mean annual precipitation (Table 4) is lower for each site along the Crater Lake transect relative to the three transects to the north. This transect also crosses the Cascade Range approximately 80 km south of any spray project conducted along the crest of the Cascades. The combined effect of these factors has resulted in a mean ΣDDT residue level (0.131 ppm) in the forest floor for this transect that is less than half the mean concentration for the other transects. Yet this residue level is considerably higher than the mean concentration of DDT in the forest floor of any of the transects across the Coast Ranges (Table 2). Aerial drift of DDT residues from the large spray projects conducted 80–322 km to the north has contributed to this level of contamination of unsprayed forests.

DDT ISOMERS AND METABOLITES

Residue levels of each isomer and metabolite of DDT in the forest floor and soil samples show essentially the same relationships and trends along transects of both mountain ranges except for TDE residues in samples from the Coast Ranges. Total residue levels were relatively low in samples from these transects, and the levels of TDE were too low to be quantified in more than half of the forest floor samples and in almost 75 percent of the soil samples from both depths. In contrast, residues of TDE could be easily quantified in over 75 percent of all samples from the Cascade Range.

TABLE 4. *Mean annual precipitation at each sampling site along transects across the Coast and Cascade Ranges in western Oregon, September–November, 1966* [1]

	Precipitation, cm				
	Distance from Coast, km				
Coast Range Transects	0	16	32	48	64
Wilson River	241	254	267	254	127
Yaquina	152	178	203	216	140
Umpqua	165	203	216	152	114
Rogue	203	229	267	216	203
	Elevation above Sea Level, Meters				
Cascade Range Transects	457	762	1067	1372	16 km E
Mt. Hood	190	203	216	229	127
Santiam Pass	267	279	305	190	89
Willamette Pass	114	152	165	165	76
Crater Lake	102	114	127	152	64

[1] Mean annual precipitation levels were estimated from U.S. Geological Survey isohyetal maps for western Oregon.

The largest proportion of all DDT residues found in samples from both sets of transects was present as *p,p'*-DDT. Residues of this isomer accounted for approximately 64 percent of the ΣDDT found in the forest floor (Table 5). The proportion of *p,p'*-DDT decreased with depth, whereas the relative amounts of *o,p'*-DDT and *p,p'*-DDE increased with depth. However, more than 80 percent of the total residues found at all sites remained in the forest floor. The relative proportions of the DDT isomers and metabolites, and the changes in relative distribution with sample depth, indicate that degradation is taking place slowly.

TABLE 5. *Mean residue levels of DDT isomers and metabolites in forest floors and soils of the Coast and Cascade Range transects expressed as a percentage of the mean ΣDDT residue level, September–November 1966*

Sample Depth, cm	*p,p'*-DDE	*o,p'*-DDT	*p,p'*-TDE	*p,p'*-DDT
COAST RANGE TRANSECTS				
Forest floor	14.93	21.35	—[1]	63.72
Soil: 0–7.5	22.38	27.31	—	50.31
Soil: 7.5–15	23.16	35.99	—	40.85
CASCADE RANGE TRANSECTS				
Forest floor	15.82	14.62	4.99	64.57
Soil: 0–7.5	19.70	26.34	4.33	49.63
Soil: 7.5–15	21.48	35.77	2.62	40.13

[1] TDE is not included because this metabolite could only be quantified in approximately 35 percent of the litter and soil samples from the Coast Range transects.

SIGNIFICANT EFFECTS OF TRANSECT, SITE, AND SAMPLING DEPTH

Residue data for each range were analyzed statistically to determine whether sampling transects or sampling

sites (distance from coast or change in elevation) significantly influenced the level of DDT residue found. A split-split plot design was used, and the data were analyzed by analysis of variance. The first stage examined the influence of subsite and site over all three sampling depths, and the second stage provided a separate analysis for each depth. In addition, residue data for the Cascade Range were analyzed by a factorial analysis of variance using a randomized complete block design.

The average ΣDDT residue over all three sampling depths increased significantly with distance inland from the coast (Table 6). Average concentrations over all depths and for all four transects were 20.0, 20.9, 26.0, 29.6, and 46.9 ppm DDT for the sampling sites at 0, 16, 32, 48, and 64 km inland, respectively. Since these means represent 240 individual samples, this upward trend is not likely to be a chance occurrence. Sampling depth and the site × depth interaction were also highly significant ($P < 0.01$). These results were not unexpected since it was anticipated that if any measurable DDT residues were found, the highest concentrations would occur in the forest floor which represents the receiving surface for any atmospheric residues brought down by precipitation. The site × depth interaction indicates that the upward trend in residues with distance inland occurs at each depth, but the trend is less pronounced at each greater sampling depth.

TABLE 6. *Statistical analysis of the influence of transect, site, and subsite over all sampling depths on the distribution of total residues of DDT in the Coast Ranges, September–November 1966*

Source	DF	Sum of Sq.	Mean Sq.	*F*-value
Total	239	300,147		
Transects	3	160	53	n.s.
Site	4	22,888	5,722	16.16**
Error (a)	12	4,250	354	
Subsite	3	230	77	n.s.
Subsite × site	12	601	50	n.s.
Error (b)	36	3,955	110	
Depth	2	215,228	107,614	286.97**
Site × depth	8	32,723	4,090	10.91**
Subsite × depth	6	483	81	n.s.
Error (c)	24	9,006	375	
Error (d)	72	7,017	97	

NOTE: ** = Differences are highly significant ($P < 0.01$); n.s. = differences are not significant ($P > 0.05$).

Analysis for each depth did not provide any additional information. The influence of site showed the same highly significant increase with distance inland for forest floor residues. This relationship was only significant ($P < 0.05$) for residues in the surface layer of mineral soil, and nonsignificant ($P < 0.05$) for residue levels in the lower soil samples.

A similar series of analyses was conducted for each DDT isomer and metabolite. Residue levels of *p,p'*-DDE, *o,p'*-DDT, and *p,p'*-DDT showed the same relationships discussed above and the same levels of significance.

Residue data for the Cascade Range transects were statistically analyzed by the same split-split plot design (Table 7). There were no significant differences among average ΣDDT levels by transect or by sites for a given transect for either forest floor or soil. However, examination of the data presented in Table 3 indicates that residue levels are generally lower at each site located 16 km east of the crest of the Cascades, and that residue levels along the Crater Lake transect are lower than those observed for each of the three transects crossing the Cascade Range closer to the old spray projects. Residue data for the forest floor samples were analyzed by a factorial analysis of variance using a randomized complete block design. Residue levels in the forest floor were significantly lower east of the Cascades, and residues along the Crater Lake transect were significantly lower than residue levels in the forest floor samples from the other three transects (both at $P < 0.01$).

TABLE 7. *Statistical analysis of the influence of transect, site, and subsite over all sampling depths on the distribution of ΣDDT residues in samples from the Cascade Range, September–November 1966*

Source	DF	Sum of Sq.	Mean Sq.	*F*-value
Total	239	15,684,060		
Transects	3	542,593	180,864	1.81 n.s.
Site	4	517,790	129,448	1.29 n.s.
Error (a)	12	1,198,556	99,880	
Subsite	3	103,352	34,451	1.22 n.s.
Subsite × side	12	290,760	24,230	0.86 n.s.
Error (b)	36	1,012,599	28,128	
Depth	2	5,048,995	2,524,498	30.93**
Site × depth	8	922,449	115,306	4.69**
Subsite × depth	6	183,554	30,592	1.24 n.s.
Error (c)	24	1,958,987	81,624	
Error (d)	72	1,771,308	24,601	

NOTE: ** = Differences are highly significant ($P < 0.01$); n.s. = differences are not significant ($P > 0.05$).

This distribution of DDT residues in unsprayed areas is consistent with similar data reported by Cory et al. (*7*). In a study of the distribution of DDT residues in the Sierra Nevada Mountains, concentrations were markedly lower east of the crest. They also reported higher and more variable residue levels in samples from locations near old spray projects conducted in 1953 and 1956.

Closer examination of the data for each subsite along the Cascade Range transects shows that residue levels from all sampling sites and depths were extremely variable. The standard deviation of the mean for ΣDDT residues in the forest floor samples from the Santiam transect is greater than the mean. The causes of this variation are most likely the relative position of the sampling sites in reference to the location of the old

spray projects and the prevailing climatic conditions at the time those 1.16 million hectares were sprayed with DDT. The one sampling site that unintentionally fell in an old spray unit greatly distorts the residue levels for that site and for the transect, but it does not account for all variation observed among and between sampling sites. This discussion applies equally to all statistical analyses conducted on the Cascade Range residue data for each depth and for each DDT isomer and metabolite.

Conclusions

The primary purposes of this study were to determine to what extent untreated forested areas in western Oregon may have become contaminated through washout of DDT residues known to be present in the atmosphere, and to establish background levels of DDT residues in forest litter and soil. Perhaps the most important result obtained is the fact that measurable quantities of DDT were found at every site sampled along each of the eight transects. Residue levels along transects across the Coast Ranges increased significantly with distance inland from the coast. This trend is readily explained in that each transect ends in a forested area adjacent to agriculturally important inland valleys or population centers which serve as a source of the pesticide residues. Residue levels along transects across the Cascade Range were considerably higher than those found in the Coast Ranges because of the influence of a number of large insect control projects conducted along the crest of the Cascades between 1949 and 1953. Distance and direction of sampling sites from these sprayed areas have produced a wide variation in residue levels which tends to mask the influence of annual rainfall distribution and other local differences in topography.

Although DDT residues were found at every point sampled, the levels of these residues were generally low. Maximum concentrations of DDT in forest floor samples from the Coast Ranges did not exceed 0.17 ppm. Residue levels in forest floor samples from the Cascade transects were generally three to five times higher than those from Coast Ranges, but mean residues still did not exceed 0.50 ppm DDT. Low levels in the surface mineral soils of both sets of transects further substantiate the fact that DDT is not readily leached into forest soils. The tenacity with which the organic horizons of forest soils hold residues of DDT strongly suggests that the levels of residue measured are not likely to become available to nontarget organisms in toxic amounts (*28*).

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FISH, WILDLIFE, AND ESTUARIES

Influence of a Local Source of DDT Pollution on Statewide DDT Residues in Waterfowl Wings, Northern Alabama, 1978–79

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ABSTRACT

Heavy DDT contamination resulting from a former DDT manufacturing plant in northern Alabama has influenced statewide averages of DDT, DDE, and TDE residues in duck wings tested in the National Pesticide Monitoring Program. In states where contaminant levels in duck wings are high, residue analyses of wings categorized by finer geographic subdivision may be useful in defining the areas of heaviest contamination.

Introduction

The Fish and Wildlife Service, U.S. Department of the Interior, began nationwide monitoring of organochlorine residues in the wings of black ducks (*Anas rubripes*) and mallards (*Anas platyrhynchos*) in 1965 as part of the National Pesticide Monitoring Program (*1*). Waterfowl wings submitted to the Fish and Wildlife Service annual Waterfowl Harvest Survey were analyzed for organochlorine residues for the years 1965–67 (*1*), 1969–70 (*2*), 1972–73 (*5*), and 1976–77 (*6*). Analyses were based on sample pools of 25 wings each with the number of pools from each state varying in proportion to the number of wings submitted from each state. Although organochlorine residues in duck wings are reported for individual states, waterfowl are migratory, and it is conceivable that these residues may not accurately reflect the relative degrees of contamination between states. However, consistent outstanding trends in residue data over several collection periods indicate that local organochlorine contamination may be recognizable by monitoring residues in duck wings.

Duck wings from Alabama consistently have shown elevated concentrations of DDT and its metabolites, in comparison to other states. Therefore, duck wings from Alabama would appear to be prime candidates for determining the usefulness of this type of monitoring in pinpointing local sources of organochlorine contamination. Alabama and California were the only states in which DDE in mallard wings exceeded 1 ppm for at least three of the five previous sampling periods. Mallard wings from Alabama had the highest average DDE residues of all states in the 1965–66 and 1969–70 surveys (*1*, *2*). In 1972, duck wings from Alabama had higher DDT and DDE residues than any other state (*5*), exceeding national averages by factors of 12.9 and 6.2, respectively. In 1976, Alabama was highest for DDT and third highest for DDE, at 3.2 and 2.6 times the national averages (*6*).

It seems likely that the high DDT and DDE concentrations observed in duck wings from Alabama were due largely to industrial contamination of their winter habitat. From 1949 to 1970, a commercial DDT manufacturing plant released its effluent into Huntsville Spring Branch, a tributary of the Tennessee River in northern Alabama. DDT and its metabolites in sediments of a 4-mile portion of Huntsville Spring Branch have been estimated at 4,000 tons (Tennessee Valley Authority, unpublished report, 1978). This heavily contaminated area and the area immediately downstream from this site are encompassed by the Wheeler National Wildlife Refuge, a major waterfowl wintering area in Alabama. The present study examines the influence of this point source of pollution on statewide averages of DDT, DDE, and TDE concentrations in duck wings. Also, the authors explore the usefulness of subclassifying duck wings by county of collection, for the purpose of identifying local sources of organochlorine pollution.

Sampling and Analysis

Mallard wings from Alabama were collected during the 1978–79 Waterfowl Harvest Survey, the same source

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of wings used for the National Pesticide Monitoring Program. Wings were sorted by county of collection and subdivided by age-sex groups. Wings sorted in this fashion were then randomly assigned to composite samples or pools of five wings each. Wings from adjacent counties were pooled in some instances to provide enough wings for analysis. Remaining wings were then combined into a northern Alabama pool or a southern Alabama pool. A total of 44 wing pools was analyzed.

Wings were shipped to Raltech Scientific Services, Inc., Madison, Wisconsin, for residue analyses. They were prepared and analyzed by the same procedure established for the Nationwide Pesticide Monitoring Program (*6*), except that the cleanup solvent was a mixture of 15 percent dichloromethane and 85 percent cyclohexane. The lower limit of quantification of DDT and its metabolites was 0.01 ppm. Percent recoveries for spiked samples were 75 for DDT, 93 for DDE, and 80 for TDE. Data were not corrected for percent recoveries.

Results and Discussion

ΣDDT in duck wings from Alabama varied considerably by region and was highest in counties near the DDT manufacturing plant (Table 1, Fig. 1). Pools of wings from Limestone and Madison Counties had ΣDDT residues that averaged 10.8 and 18 times higher, respectively, than the combined average of all other counties or county groups ($P < 0.05$). Heaviest contamination appeared to be localized in these two counties; residues in adjoining counties were not greatly elevated (Fig. 1). The former DDT manufacturing site is in Madison County, 15 km east of Limestone County. Wheeler National Wildlife Refuge is located in Madison, Limestone, and Morgan Counties. Pollution from the DDT plant therefore seems to be the likely source of the high ΣDDT concentrations in waterfowl from Madison and Limestone Counties. Waterfowl banding records show that mallards harvested in Madison and Limestone Counties are not members of a nesting population that is distinct from that of the rest of the state. Therefore, the common link for contaminated birds is their wintering area and not their breeding grounds.

The high mean concentrations of DDT, DDE, and TDE observed in duck wings from Alabama during previous monitoring studies (*1, 2, 4, 6*) have undoubtedly been strongly influenced by this localized contamination; a large proportion of the total number of mallard wings from Alabama was submitted from the northern quarter of the state and 5–35 percent came from Limestone and Madison Counties (Table 2). Limestone, Madison, and Morgan Counties accounted for 27–50 percent of the wings submitted during each of the sampling years. The highest residue concentrations during the five sampling periods of the National Pesticide Monitoring Program (Table 3) occurred when the greatest proportion of wings was harvested in areas in northern Alabama (Table 2).

The lowest statewide residues of ΣDDT occurred when the proportion of wings from Madison and Limestone Counties was lowest. Otherwise there are no apparent simple correlations between specific residue means and proportions of the harvest taken from various areas in northern Alabama. This lack of correlation is undoubtedly due to the small number of pools analyzed each year and the high variation between pools (Table 3). Such variation may be caused by very high residues in a few individuals of a sample pool. For example, if 24 wings in a pool contained 1 ppm ΣDDT and a single wing contained 101 ppm ΣDDT, then the sample pool residue would be 5 ppm. Authors have previously reported residues of up to 480 ppm ΣDDT in mallard carcasses from Huntsville Spring Branch (*4*); therefore, it is likely that extremely high residues in a few wings would contribute materially to the great variation seen in past monitoring studies (Table 3).

The distribution of mallards and black ducks and the proportion of ducks harvested in different localities within a state determine the effectiveness of using organochlorine residues in duck wings to pinpoint polluted environments. States where organochlorine residues in waterfowl wings are above the national average may have waterfowl harvests occurring in contaminated environments. Thus residue analyses of duck wings might be useful in pinpointing local areas of contamination if areas of wing collection are defined by subclassification below the state level. Authors conclude from the present study that the use of duck wings to locate areas of contamination within a state show the greatest promise when residues in composite sample pools from various states are known to be much higher than national averages.

Finally, comparison of the present data with those of experimental studies of black ducks fed DDE (*3*) indicates that the local DDT contamination detected by the present study in Alabama may have serious implications for the reproductive health of waterfowl wintering in this area. Longcore and Stendell (*3*) provided data suggesting that DDE residues of 2–3 ppm in wings can be correlated with eggshell thinning and decreased productivity in female black ducks. DDE residue concentrations exceeded 3 ppm in 6 of 15 pools from Limestone County; in one pool it reached 10 ppm (Tabe 1) but concentrations of DDE may have been slightly overestimated compared to those reported by Longcore and Stendell (*3*) because of possible differences in moisture loss. Although residues in female mallards from Limestone and Madison Counties were less than for males, fewer pools of wings from females

TABLE 1. *DDT, DDE, and TDE residues in pools of mallard wings from Alabama, 1978–79 hunting season* [1]

Designation [2]	County	Statistic	Residues, ppm Wet Weight											
			Immature Females			Immature Males			Adult Females			Adult Males		
			DDE	DDT	TDE	DDE	DDT	TDE	DDE	DDT	TDE	DDE	DDT	TDE
1	Lauderdale,	Mean±SD	0.32	0.02	0.02	—	—	—	0.31	ND	ND	—	—	—
	Colbert,	Range	—	—	—	—	—	—	—	—	—	—	—	—
	Lawrence	*N*	1	1	1	—	—	—	1	1	1	—	—	—
2	Limestone	Mean±SD	0.76±0.50	0.03±0.01	0.16±0.20	0.87±1.20	0.05±0.08	0.12±0.17	0.02	ND	ND	4.40±5.10	0.90±0.75	1.80±0.47
		Range	0.40–1.10	0.02–0.04	0.01–0.31	0.16–2.70	0.01–0.17	0.02–0.38	—	—	—	0.11–10.0	0.37–1.40	1.50–2.10
		N	2	2	2	4	4	4	1	1	1	3	3	3
3	Madison	Mean±SD	2.60±3.20	0.21±0.29	0.62±0.71	1.40±0.52	2.70±2.60	0.74±0.98	—	—	—	5.61	0.07	0.41
		Range	0.37–4.80	0.00–0.41	0.12–1.12	1.00–1.70	0.79–4.50	0.04–1.40	—	—	—	—	—	—
		N	2	2	2	2	2	2	—	—	—	1	1	1
4	Jackson,	Mean±SD	0.49	0.03	0.00	—	—	—	0.21	0.09	0.03	0.26±0.06	0.15±0.02	0.03±0.03
	Marshall,	Range	—	—	—	—	—	—	—	—	—	0.21–0.33	0.00–0.03	0.01–0.05
	Morgan	*N*	1	1	1	—	—	—	1	1	1	2	2	2
5	Green,	Mean±SD	—	—	—	0.44±0.44	0.03±0.04	0.01±0.01	—	—	—	—	—	—
	Sumter,	Range	—	—	—	0.13–0.75	0.00–0.06	0.00–0.01	—	—	—	—	—	—
	Choctaw	*N*	—	—	—	2	2	2	—	—	—	—	—	—
6	Clarke,	Mean±SD	0.03	0.00	0.00	0.02	0.00	0.00	0.07	0.00	0.00	0.16±0.02	0.01±0.01	0.00
	Wilcox,	Range	—	—	—	—	—	—	—	—	—	0.14–0.17	0.00–0.01	0.00–0.00
	Washington	*N*	1	1	1	1	1	1	1	1	1	2	2	2
7	Mobile,	Mean±SD	—	—	—	0.06	0.00	0.00	—	—	—	0.18	0.01	0.00
	Baldwin	Range	—	—	—	—	—	—	—	—	—	—	—	—
		N	—	—	—	1	1	1	—	—	—	1	1	1
	Northern	Mean±SD	0.25	0.45	0.11	0.80±0.82	0.35±0.46	0.12±0.12	0.61±0.74	0.06±0.07	0.02±0.02	—	—	—
	County	Range	—	—	—	0.23–1.70	0.02–0.87	0.03–0.24	0.09–1.13	0.01–0.11	0.00–0.03	—	—	—
	Pool	*N*	1	1	1	3	3	3	2	2	2	—	—	—
	Southern	Mean±SD	0.08±0.02	0.00	0.00	—	—	—	0.07	0.00	0.00	—	—	—
	County	Range	0.06–0.09	0.00–0.00	0.00–0.00	—	—	—	—	—	—	—	—	—
	Pool	*N*	2	2	2	—	—	—	1	1	1	—	—	—
	Controls [3]	Mean±SD	0.05±0.04	0.01±0.01	0.01±0.01									
		Range	0.01–0.11	0.00–0.02	0.00–0.03									
		N	5	5	5									

NOTE: SD = standard deviation; ND = not detected.

[1] Each pool consisted of five wings.

[2] See Figure 1.

[3] Control wing pools consisted of wings from five juveniles, without regard to sex. Wing were obtained from pen-raised mallards.

were sampled. Authors have found carcass residues of 480 ppm ΣDDT in female mallards from Wheeler National Wildlife Refuge (*4*), indicating that females also may have high ΣDDT residues.

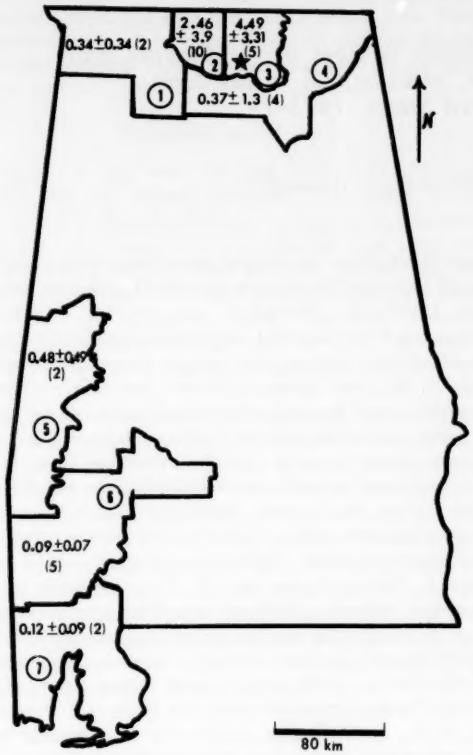

FIGURE 1. *ΣDDT residues in mallard wings from Alabama, 1978–79. Mean ± 1 standard deviation in ppm wet weight for pools of five wings. Number of pools are indicated in parentheses; encircled numbers refer to the county key in Table 1. Star shows location of former DDT manufacturing plant.*

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TABLE 2. *Number of mallard wings submitted from selected areas in Alabama during five years of the National Pesticide Monitoring Program, 1965–76*

Area	Year									
	1965		1966		1969		1972		1976	
	N	%[1]	N	%	N	%	N	%	N	%
Madison and Limestone Counties	27	17	96	35	3	5	60	29	126	23
Madison, Limestone and Morgan Counties	54	34	137	50	16	28	67	33	108	27
Northern quarter of state	100	64	193	71	29	51	140	69	307	67
Entire state	157	100	271	100	57	100	202	100	460	100

[1] Percentage of the total number of wings submitted from Alabama for the year indicated.

TABLE 3. *DDE, DDT, and TDE residues in composite samples of mallard wings from Alabama for the first five years of the National Pesticide Monitoring Program, 1965–76* [1]

Chemical	Statistic	Year				
		1965	1966	1969	1972	1976
DDE	Mean ± SD	0.76	2.62	1.75	1.85 ± 1.53	0.69 ± 0.34
	Range	0.43–5.31 [2]		—	0.79–4.12	0.17–2.39
	N	5	6	1	4	6
DDT	Mean ± SD	0.30	0.35	0.09	1.03 ± 1.31	0.19 ± 0.06
	Range	—	—	—	0.23–2.98	0.01–0.41
	N	5	6	1	4	5
TDE	Mean ± SD	0.11	0.56	2.07	0.44 ± 0.53	0.38 ± 0.33
	Range	—	—	—	0.09–1.23	<0.01–1.72
	N	5	6	1	4	5

[1] Each composite sample consisted of 25 wings.
[2] Range for 1965 and 1966 data combined.

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Organochlorine Residues and Shell Thicknesses in Eggs of the Clapper Rail, Common Gallinule, Purple Gallinule, and Limpkin (Class Aves*), Eastern and Southern United States, 1972–74*

Erwin E. Klaas,[1] Harry M. Ohlendorf,[2] and Eugene Cromartie [2]

ABSTRACT

Organochlorine residues and shell thicknesses were surveyed in eggs of the clapper rail (Rallus longirostris), *purple gallinule* (Porphyrula martinica), *common gallinule* (Gallinula chloropas), *and limpkin* (Aramus guarauna) *from the eastern and southern United States. Clapper rail eggs were collected during 1972–73 in New Jersey, Virginia, and South Carolina. During 1973–74, gallinule eggs were collected in Florida, South Carolina, and Louisiana, and limpkin eggs were collected in Florida. Egg contents were analyzed for residues of organochlorine pesticides, including DDT, TDE, DDE, dieldrin, mirex, heptachlor epoxide, oxychlordane,* cis*-chlordane (and/or* trans*-nonachlor),* cis*-nonachlor, hexachlorobenzene (HCB), toxaphene, and endrin, and for polychlorinated biphenyls (PCBs). Shell thicknesses of recent eggs of these species were compared with archival eggs that had been collected before 1947. With the exception of the limpkin, the majority of eggs analyzed contained residues of* p,p'*-DDE and PCBs. Geometric means ranged from 0.10 ppm to 1.3 ppm. Small amounts (<1.0 ppm) of mirex, dieldrin,,* cis*-chlordane (and/or* trans*-nonachlor), TDE, and DDT were detected in a few eggs. No evidence of eggshell thinning was found for any of the species studied. DDE residues in clapper rail eggs were higher in New Jersey and Virginia than in South Carolina.*

Introduction

Organochlorine compounds are well known as persistent environmental contaminants that tend to accumulate in the upper trophic levels of food chains. The occurrence of organochlorine residues in tissues of carnivorous animals and the effects of these contaminants on their reproduction, behavior, and survival has been extensively documented (*14, 16*). However, residues in animals at intermediate levels of food chains are less well known.

Authors report here the results of a survey of residues and shell thicknesses in eggs of four species of the avian order Gruiformes: the clapper rail (*Rallus longirostris*), purple gallinule (*Porphyrula martinica*), common gallinule (*Gallinulla chloropas*), and limpkin (*Aramus guarauna*). Environmental contaminants in these species are of interest because they occupy intermediate positions in the food chains of North American wetland ecosystems, and because rails and gallinules are hunted as game and consumed by humans in many areas. Several species or subspecies of Gruiformes have also been designated as endangered, including the whooping crane (*Grus americana*), Mississippi sandhill crane (*Grus canadensis pulla*), California clapper rail (*Rallus longirostris obsoletus*), light-footed clapper rail (*R. l. levipes*), Yuma clapper rail (*R. l. yumanensis*), and Hawaiian gallinule (*Gallinula chloropus sandvicensis*) (*17*). Moreover, the limpkin, whose distribution in the United States is limited to Florida, has been designated by that state as endangered. It feeds almost exclusively on large freshwater snails, mainly the apple snail (*Pomacea paludosa*) (*12*). This snail is considered also to be the sole source of food for the endangered Everglade kite (*Rostrhamaus sociabilis*) (*3*).

Small amounts of dieldrin (<0.04 ppm), *p,p'*-DDT (<0.06 ppm), *p,p'*-TDE (<0.02–0.59 ppm), and *p,p'*-DDE (0.06–0.20 ppm), have been reported in tissues of the endangered whooping crane (*11*), but eggshell thickness has remained normal in this species (*2*). Notably high levels of dieldrin were found in eggs of purple gallinule and common gallinule collected from rice fields in Louisiana (*5, 9*). However, egg hatchability, chick survival, and eggshell thickness for gallinules nesting in rice fields did not differ significantly from gallinules nesting in marsh areas where residue levels were much lower.

Flickinger and King (*7*) reported 20.0 ppm and 5.5 ppm dieldrin and 21.0 ppm and 1.2 ppm DDT and metabolites in carcasses of two king rails (*Rallus elegans*) in Texas. The carcass of a common gallinule collected in the same area contained only 0.1 ppm ΣDDT and <0.1 ppm dieldrin. Residue levels in one of the king rails

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were among the highest and those in the gallinule were among the lowest reported in 62 specimens of birds representing 32 species found dead near aldrin-treated rice fields during 1967–71. Foehrenbach et al. (*8*) reported a mean of 0.38 ppm DDT and metabolites in four clapper rail eggs from Long Island, New York. Authors know of no other published data on organochlorine residues and eggshell thickness among gruiform birds.

Sampling and Analysis

Clapper rail eggs were collected during 1972–73 from Cape May and Atlantic Counties, New Jersey; Accomack and Northampton Counties, Virginia; and Charleston County, South Carolina. Gallinule eggs were collected during 1972–73 from Brevard, Glades, Lee, and Marion Counties, Florida; Beaufort County, South Carolina; and Cameron Parish, Louisiana. Limpkin eggs were collected during 1973–74 from the northwest side of Lake Okeechobee, Glades County, Florida.

Complete clutches and addled eggs were collected; two eggs from each clutch were wrapped in aluminum foil and placed in plastic containers to retard moisture loss. Eggs were refrigerated until the contents were removed, placed into chemically cleaned jars, and frozen pending chemical analysis. Only one egg per clutch was analyzed, but shells of all eggs were saved for comparisons of shell thickness. Egg volumes were measured to the nearest 1.0 ml by water displacement before the contents were removed. This allowed residues to be adjusted to fresh wet weight, assuming specific gravity of 1.0 as suggested by Stickel et al. (*15*).

Egg contents were homogenized in a mixer, and a 10-g aliquot was blended with sodium sulfate and extracted 7–8 hours with hexane in a Soxhlet apparatus. Cleanup of the extract, and separation and quantitation of organochlorines were similar to the procedures used for the analysis of eagle carcasses (*6*). In summary, the concentrated hexane extract was placed on a Florisil column and eluted with 200 ml of 6 percent ethyl ether in hexane to remove lipids. The Florisil eluate was concentrated and eluted from a silicic acid column to separate pesticides from polychlorinated biphenyls (PCBs). The organochlorines separated into three silicic acid eluates were identified and quantitated by electron-capture gas chromatography on a 1.83-m glass column packed with a mixture of 4 percent SE-30 and 6 percent QF-1 on 100–120-mesh Supelcoport. Pesticides were quantitated with a computing integrator; PCBs were quantitated by comparing total peak area with that of Aroclor 1254 or 1260, whichever most closely resembled the gas chromatographic profile of the sample. Residues in about 10 percent of the samples were confirmed by gas chromatography-mass spectrometry.

Samples were analyzed for DDT, TDE, DDE, dieldrin, mirex, heptachlor epoxide, oxychlordane, *cis*-chlordane (and/or *trans*-nonachlor), *cis*-nonachlor, hexachlorobenzene (HCB), toxaphene, endrin, and PCBs.

Recoveries of pesticides and PCBs from spiked egg tissue ranged from 83 percent to 104 percent. Residues in the present report were not adjusted on the basis of these recoveries. Sensitivity of detection was 0.1 ppm for pesticides and 0.5 ppm for PCBs. When PCBs were detected in trace amounts (<0.5 ppm), they were considered as 0.25 ppm for purposes of this report. Chemical residue values were transformed to their common logarithms for statistical analysis. A unit of 1.0 was added to each value prior to transformation, to accommodate zero values. Total lipids averaged 8.7 percent in clapper rail eggs, 8.8 percent in limpkin, 10.2 percent in purple gallinule, and 10.4 percent in common gallinule.

For studies of shell thickness, the eggs collected for residue analyses were supplemented by eggs from museum collections. Authors compared shell thicknesses of egg collected since 1946 with shell thicknesses of eggs collected before the widespread use of organochlorine pesticides. Shell thickness was measured to the nearest 0.01 mm with a modified Starrett micrometer after the shells had dried at room temperature for at least one month. Three measurements were taken at the equator of each egg and included the shell and shell membranes. Measurements were averaged to yield a single value for each egg in the clutch, and values for all eggs in a clutch were averaged to yield a clutch mean thickness, the basic unit of measurement for statistical treatment.

For each species, eggshell thickness data for various geographic localities were grouped into time periods pre-1947 and 1947–74. Variations among localities and time periods were subjected to two-way, nonrandom analysis of variance (ANOVA). Statistical testing of differences in mean thicknesses between time periods and geographic locations followed the procedures of Sokal and Rohlf (*13*).

Results and Discussion

CLAPPER RAIL

All 49 eggs analyzed contained *p,p'*-DDE, but mean residue levels were relatively low (Table 1). A mean value of 1.3 ppm in New Jersey eggs was more than three times as high as the mean for eggs from South Carolina. Mean residue levels for Virginia and New Jersey eggs are not significantly different but both are significantly higher than the mean for South Carolina eggs ($P < 0.05$, ANOVA, log-transformed data). Residues of PCBs occurred in 100 percent of the samples

TABLE 1. *DDE and PCB residues in eggs of the clapper rail, purple gallinule, common gallinule, and limpkin from eastern United States, 1972–73*

Locality	Organochlorine	n [1]	ppm, Wet Wt: Geom. Mean	Median	Range	Number with Residues
CLAPPER RAIL						
South Carolina	DDE	10	0.41	0.52	0.10–1.1	10
	PCB	10	<0.5	<0.5	ND–1.2	6
Virginia	DDE	19	0.97	1.0	0.31–2.6	19
	PCB	19	<0.5	<0.5	ND–2.1	16
New Jersey	DDE	20	1.3	1.2	0.47–6.4	20
	PCB	20	<0.5	<0.5	<0.5 –2.7	20
PURPLE GALLINULE						
Florida	DDE	10	0.18	0.13	ND–0.95	6
South Carolina	DDE	1	0.29	—	—	1
COMMON GALLINULE						
Florida	DDE	15	0.21	0.13	ND–0.80	11
Louisiana	DDE	9	<0.10	0.0	ND–0.10	2
South Carolina	DDE	1	0.24	—	—	1
LIMPKIN						
Florida	DDE	14	0.18	0.0	ND–5.6	4

NOTE: ND = not detected.
[1] Number of clutches represented.

from New Jersey, 84 percent from Virginia, and 60 percent from South Carolina. Mean values for PCBs were < 0.5 ppm for all three localities.

No organochlorine residues other than DDE and PCBs were detected in eggs from South Carolina. Mirex (0.83 ppm) was found in one egg from Accomack County, Virginia, and 0.09 ppm dieldrin and a trace of *trans*-nonachlor were found in another egg from that locality. In New Jersey samples, trace amounts (< 0.10 ppm) of *trans*-nonachlor occurred in nine eggs; mirex was detected in five eggs (mean = 0.34 ppm; range 0.16–0.45 ppm); TDE in three eggs (mean = 0.30 ppm; range 0.20–0.35 ppm); and DDT in one egg (0.25 ppm). Heptachlor epoxide, oxychlordane, *cis*-nonachlor, HCB, toxaphene, and endrin were not detected in any clapper rail eggs analyzed.

Although authors were unable to collect recent samples of clapper rail eggs from Florida for residue analysis, nine clutches (six from the west coast and three from the east coast of Florida) that had been collected after 1946 were present in museum collections. These nine clutches were used in the present comparisons of mean eggshell thicknesses (Table 2).

Within each locality, there were no significant differences ($P > 0.05$ ANOVA) between mean eggshell thicknesses for the two selected time periods (Table 2). However, significant differences ($P < 0.05$) did occur in shell thicknesses between geographic localities; eggshells from Virginia and New Jersey were thicker than those from the southern states. These observed geographic differences probably reflect

TABLE 2. *Variations in shell thicknesses of clapper rail eggs from eastern United States, 1863–1973*

Locality	1863–1946: n [1]	Mean Th, mm [2]	1947–1973: n	Mean Th, mm	% Change	1863–1973: n	Combined Mean Th, mm [3]
Florida (west)	38	0.241	3	0.242	0	41	0.241 A
Florida (east)	55	0.244	6	0.257	+5	61	0.245 A
Georgia, Carolinas	63	0.241	7	0.247	+2	70	0.242 A
Virginia	57	0.258	22	0.262	+2	79	0.259 B
New Jersey	25	0.260	18	0.255	−2	43	0.258 B

NOTE: No significant differences (ANOVA, $P > 0.05$) were detected between pre-1947 and recent eggs.
[1] n = Number of complete clutches.
[2] Means for each locality calculated from clutch mean thickness. Estimated variance (S^2) = 0.000282602 with 274 degrees of freedom.
[3] Among localities, combined means which are not significantly different share common letters (SNK test, $P > 0.05$).

environmental differences in the localities or genetic differences between species which inhabit these areas. Virginia and New Jersey are within the range of the northern clapper rail (*R. l. crepitans*). Localities in Georgia, North Carolina, South Carolina, and the east coast of Florida are within the range of the Wayne clapper rail (*R. l. waynei*). The west coast of Florida is occupied by the Florida clapper rail (*R. l. scottii*) (*1*). Accordingly, the northern clapper rail has thicker eggshells than the other two subspecies. Even with these relatively large numbers of eggs from museum collections, the authors lacked samples for many individual years and localities, especially the period from 1940 to 1971 and years prior to 1895. Authors attempted to examine variation in eggshell thicknesses among time periods of shorter duration than those given in Table 2, but results were inconclusive because gaps in the data precluded statistical testing.

Clutch sizes in clapper rails averaged 8.5 eggs (range 5–13) for 237 clutches of pre-1947 eggs and 8.6 (range 5–13) for 56 clutches of recent eggs.

No significant correlations were found between shell thickness and DDE ($r = -0.08$) or PCBs ($r = 0.04$), but a significant correlation was detected between DDE and PCBs ($r = 0.38$, $P < 0.01$).

L. J. Blus (Patuxent Wildlife Research Center, personal communication, 1975) collected seven clapper rail eggs, one from each of seven nests, from Charleston County, South Carolina in 1971. DDE in these eggs averaged 1.53 ppm (geometric mean; unpublished data). The difference in mean DDE residues between 1971 and 1972 (Table 1) is significant ($P < 0.05$) and the decline is consistent with observed declines in DDE residues in eggs of brown pelicans (*Pelecanus occidentalis*) from the same locality during 1969–73 (*4*). Sharp declines in DDE residues in clapper rail tissues and other aquatic fauna from New Jersey have also been reported (*10*).

PURPLE GALLINULE

DDE was the only organochlorine residue detected in eggs of purple gallinules, and levels were low (Table 1). A series of 89 clutches of eggs collected in Florida between 1885 and 1940 averaged 0.218 mm in thickness, and 15 clutches collected in 1948, 1962, and 1973 averaged 0.213 mm. The difference between clutches collected pre-1947 and post-1947 is not significant ($P > 0.05$). Authors had insufficient samples of recent eggs of this species from other localities to compare their shell thicknesses. However, 45 clutches of pre-1947 eggs from South Carolina had a mean thickness of 0.210 mm, and 13 clutches from Louisiana averaged 0.214 mm. Clutch sizes in the purple gallinule averaged 6.0 eggs (range 4–10) for 147 clutches of pre-1947 eggs and 5.9 (range 4–9) among 15 clutches of recent eggs.

COMMON GALLINULE

DDE was the only organochlorine residue detected in eggs of the common gallinule with the exception of one egg from South Carolina which contained 0.12 ppm mirex. Incidence of occurrence and mean residue levels were obviously lower in Louisiana than in Florida (Table 1).

Sufficient samples of recent eggs were available for comparison of shell thicknesses from only three regions (Table 3). Mean differences between time periods were not significant ($P > 0.05$) for any of the three areas. However, geographic differences in mean thickness did occur (Table 3). The pattern of differences is similar to that for the clapper rail: eggs from the southern states have thinner shells than those from the northeast. However, common gallinules have not been differentiated into more than one subspecies in the United States.

TABLE 3. *Variation in shell thickness of common gallinule eggs from eastern United States, 1884–1973*

	1884–1946		1947–1973			1884–1973	
States	n [1]	Mean Th, mm [2]	n	Mean Th, mm	% Change	n	Combined Mean Th, mm [3]
Georgia, South Carolina	17	0.268	4	0.275	+2	21	0.269 A
Florida	39	0.276	23	0.281	+2	62	0.278 B
Illinois, Iowa, Wisconsin	27	0.280	0	—	—	27	0.280 ABC
Louisiana, Texas	4	0.284	9	0.287	+1	13	0.286 BCD
Ohio, Michigan	29	0.288	0	—	—	29	0.288 CD
Massachusetts, New Jersey, New York, Virginia, Pennsylvania [4]	57	0.294	0	—	—	57	0.294 D

NOTE: No significant differences (ANOVA, $P > 0.05$) were detected between pre-1947 and recent eggs.
[1] n = Number of clutches.
[2] Thickness means for each locality calculated from clutch mean thickness. Estimated variance (S^2) = 0.000313214 with 199 degrees of freedom (ANOVA).
[3] Among localities, combined means which are not significantly different share common letters (SNK test, $P > 0.05$).
[4] Forty-eight clutches were from Pennsylvania and New Jersey.

Clutch sizes in the common gallinule averaged 7.8 eggs (range 4–14) for 173 clutches of pre-1947 eggs and 6.7 (range 5–9) among 36 clutches of recent eggs.

LIMPKIN

DDE was detected in only four of 14 clutches of limpkin eggs, and no other organochlorine residues were found in any eggs. One of the four eggs contained 5.6 ppm DDE, but the other three contained 0.23, 0.14, and 0.12 ppm. These low residues are consistent with reported low residues of DDE in apple snails (*9*).

A series of 124 clutches of limpkin eggs collected in Florida between 1882 and 1946 averaged 0.360 mm in thickness; in 151 clutches collected after 1947, shell thickness averaged 0.357 mm. The difference in means is not significant ($P > 0.05$). Of the 151 recent clutches, 100 were collected during 1950 in Dade and Indian River Counties and averaged 0.357 mm. Using analysis-of-variance procedures, no significant differences in shell thickness means were detected in comparisons of limpkin eggs on a yearly or decade basis, and no differences in thickness were found among eggs in different stages of incubation, among eggs of various clutch sizes, or among complete and incomplete clutches.

Clutch sizes of the limpkin averaged 5.5 eggs (range 3–7) for 124 clutches of pre-1947 eggs and 5.3 (range 3–7) among 151 recent clutches.

Conclusions

Eggs of clapper rail, common gallinule, purple gallinule, and limpkin (representing 139 clutches collected in the eastern United States during the early 1970s), contained low residues of DDE and PCBs, with geometric means ranging from <0.10 ppm to 1.3 ppm. Small amounts (<1.0 ppm) of mirex, dieldrin, *cis*-chlordane (and/or *trans*-nonachlor), TDE, and DDT were detected in a few eggs. Heptachlor epoxide, oxychlordane, *cis*-nonachlor, HCB, toxaphene, and endrin were not detected. No changes in eggshell thickness between time periods were evident in any of the four species. Geographic differences in thickness means were found in eggs of clapper rail and common gallinule.

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Mercury Levels in Waterfowl from Manitoba, Canada, 1971–72

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ABSTRACT

From two locations in Manitoba suspected of mercury pollution, waterfowl were collected during 1971 and 1972 to determine the incidence and nature of the contamination. Total mercury concentrations averaged 0.18 ppm and 0.22 ppm in breast muscle of 169 adult dabbling (Anatini) *and 77 adult diving ducks* (Aythyini, Mergini, *and* Oxyurini), *respectively. Mercury concentrations in breast muscles of immature ducks of these tribes averaged 0.15 ppm total mercury for 70 dabblers and 0.16 ppm for 40 divers. Mean mercury residues in livers were 0.54 ppm and 0.31 ppm, respectively, in 60 adults and 30 immature dabblers and 0.93 ppm and 0.29 ppm, respectively, in 31 adults and 15 immature divers. Primary feathers of 20 adult and 12 immature dabblers collected in the Saskatchewan River Delta averaged 2.67 ppm and 1.34 ppm, while 10 adult and 7 immature divers averaged 1.48 ppm and 1.11 ppm, respectively. Only in 20 ducks, 10 dabblers and 10 divers, did mercury concentrations in the breast muscle exceed 0.50 ppm. Statistically significant relationships for the concentration of mercury in feathers to breast muscle, feathers to liver, and breast muscle to liver were found for spring adults and for immature dabbling ducks. The only significant relationship for divers was feather to liver concentrations for immature ducks and breast muscle to liver concentrations of spring adults in 1972 in the Saskatchewan River Delta.*

Introduction

In 1970, Fimreite (*5*) predicted that industrial, domestic, and natural sources of mercury had the potential to seriously contaminate aquatic habitats in Canada. Subsequent studies have verified this prediction, as shown in the following taxa: freshwater fish (*1, 7, 8, 20, 22, 23, 32, 34*), waterfowl (*1, 5, 6, 8, 21, 33, 34, 35*), marine mammals (*9, 10, 19, 21, 22, 24, 26, 27*), and freshwater invertebrates (*12, 13, 25*).

Guidelines were established in 1970 by the Canadian Food and Drug Directorate which banned the sale of edible portions of fish containing in excess of 0.50 ppm mercury (wet weight). Therefore, in Manitoba, 356 ducks were collected during 1971 and 1972 to ascertain whether they contained elevated mercury levels (> 0.50 ppm). Some of the lakes, streams, and marshes of Manitoba may have received mercury inputs from Saskatchewan via the Saskatchewan River (*5, 36*), from Ontario via the English-Winnipeg River (*5*), and from the United States via the Red River, as well as from sources within the province.

The present study was undertaken because studies on mercury residue levels in Canadian prairie ducks (*33*) did not adequately cover Manitoba. Of 210 ducks collected, only 11 were from Manitoba and provided minimal information on potential mercury contamination of areas in Manitoba. In addition to our main concern regarding elevated mercury levels as a potential health hazard, the authors wish to document the concentration of mercury in various tissues of spring and fall migrating waterfowl and the concentration of mercury in waterfowl reared in Manitoba and to determine relationships useful in predicting concentrations of mercury in the liver and breast muscle of waterfowl.

Experimental

STUDY AREA, MATERIALS, AND METHODS

Waterfowl used in total mercury analyses were shot with 12-gauge shotgun on marshes from the Saskatchewan River Delta east of the Pas, Manitoba (Rat Hunting Creek, Summerberry River, Hill Island, Head River, Two Islands, Tom Lamb Wildlife Management Area, Little Frog Creek, and Grand Rapids) and from the Lake Winnipeg Area (Netley Marsh, Riverton, Hodgson, Hecla Island, Stead, Pine Falls, and Gypsumville). These areas were selected because of the occurrence of mercury-contaminated fish (*23*; A. J. Derksen, unpublished data) and the presence of marshes which are important to duck reproduction.

SAMPLING

To compare mercury in liver and breast muscle tissues, 136 ducks were collected. In addition to these tissues, primary feathers were obtained from 49 of the speci-

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[2] Fisheries Research Division, Department of Mines, Natural Resources and Environment, 1495 St. James Street, Winnipeg, Manitoba, Canada R3H OW9.

mens for mercury analysis. The samples were distributed as follows: 42 ducks in 1971 and 50 in 1972 were collected from the Saskatchewan River Delta. Also in 1971, 44 ducks were collected from the Lake Winnipeg area. Approximately half the samples were collected during April and early May; the remainder were collected during late August in the Saskatchewan River Delta and during October and early November in the Lake Winnipeg area. An additional 220 ducks, from which only breast muscle was taken for analysis, were collected over the two-year period from both areas.

Immature refers to young of the year collected on either natal areas or areas adjacent to natal sites.

TISSUES

The breast muscle, weighing approximately 20 g, was dissected from the left side of the keel of each frozen specimen. A minimum of 10 g sample of liver tissue was removed from the left lobe. Tissue samples were wrapped in aluminum foil, stored in jars, and kept frozen until analysis. The sixth through tenth primary feathers, usually from the left wing, were stored in envelopes until analysis. Before storage, feathers were cleaned according to the method of Kelsall (*18*).

RESIDUE ANALYSIS

Breast muscle, liver, and feather samples from the two study areas were analyzed by the Environmental Management, Winnipeg. Mercury was determined by flameless atomic absorption spectrophotometry (*2*). The method was slightly modified: Only 10 mL $KMnO_4$ reagent was necessary to digest duck flesh. The method was reliable within ±10 percent of the actual value (*6*) and our spiked samples showed total recovery. All values are given as total mercury on a ppm wet weight basis.

Arithmetic means are presented throughout the text for convenience, but statistical comparison of laboratory results were made by the nonparametric Mann-Whitney U method (*28*).

Results and Discussion

RESIDUES IN BREAST MUSCLE

Low concentrations of mercury (Table 1) were found in the breast muscle of adult ducks collected during spring 1971 and 1972 from the Saskatchewan River Delta. Average value for both years was 0.10 ppm mercury for 110 dabbling ducks and 0.19 ppm for 52 diving ducks. The concentration of mercury in breast muscle of dabblers from Lake Winnipeg was comparable at 0.16 ppm ($n = 17$), while mercury concentration in divers was significantly higher [Mann-Whitney U test (*28*), $P < 0.05$] at 0.43 ppm ($n = 7$).

TABLE 1. *Mercury levels in the breast muscle of 16 species of waterfowl collected in Manitoba during 1971 and 1972*

Species/ Season/Age	ppm Hg Wet Wt					
	Saskatchewan River Delta			Lake Winnipeg		
	Number	Mean	Range	Number	Mean	Range
Mallard						
Spring 1971	12	0.17	0.05–0.45	2	0.11	0.03–0.18
1972	19	0.12	0.02–0.42			
Fall 1971 Im	11	0.12	0.04–0.48	6	0.12	0.06–0.19
1971 Ad	3	0.06	0.03–0.09	6	0.16	0.08–0.23
1972 Im	10	0.19	0.07–0.30			
1972 Ad	7	0.12	0.05–0.22			
Pintail						
Spring 1971	1	0.04		2	0.11	0.10–0.12
Fall 1971 Im	2	0.15	0.14–0.16	3	0.17	0.04–0.23
Gadwall						
Spring 1971	10	0.05	0.02–0.08	1	0.04	
Fall 1971 Im	9	0.07	0.04–0.11			
1971 Ad	2	0.08	0.06–0.11			
1972 Ad	1	0.13				
American wigeon						
Spring 1971	10	0.06	0.02–0.08			
1972	1	0.04				
Fall 1971 Im				3	0.06	0.05–0.08
1971 Ad	3	0.07	0.04–0.08	2	0.03	0.02–0.05
1971 Ad	1	0.66				
American green winged teal						
Spring 1971	3	0.08	0.06–0.11	3	0.08	0.04–0.12
1972	10	0.18	0.12–0.23			
Fall 1971 Im				5	0.18	0.09–0.22
1971 Ad	2	0.30	0.06–0.54			
1972 Im	2	0.25	0.12–0.39			
1972 Ad	1	0.33				
Blue-winged teal						
Spring 1971	12	0.26	0.06–0.65	6	0.20	0.08–0.31
1972	20	0.23	0.10–0.35			
Fall 1971 Im	1	0.18		3	0.53	0.44–0.62
1971 Ad	5	0.13	0.09–0.19	3	0.49	0.12–0.76
1972 Im	11	0.09	0.05–0.16			
1972 Ad	2	0.16	0.13–0.19			
Shoveler						
Spring 1971	11	0.35	0.15–0.51	3	0.29	0.20–0.39
1972	1	0.37				
Fall 1971 Im	3	0.12	0.10–0.15			
1971 Ad	2	0.19	0.13–0.25	1	0.28	
1972 Im	1	0.13				
1972 Ad	1	0.74				
Redhead						
Fall 1971 Im	1	0.12		1	0.10	
1971 Ad				1	0.04	
Canvasback						
Spring 1971	7	0.08	0.05–0.12			
Fall 1971 Im	8	0.09	0.02–0.26			
1971 Ad				1	0.02	
1972 Im	1	0.12				
Greater scaup						
Fall 1971 Im	2	0.20	0.12–0.27			
Lesser scaup						
Spring 1971	13	0.16	0.08–0.33	3	0.32	0.08–0.76
1972	21	0.19	0.06–0.70			
Fall 1971 Im	5	0.19	0.11–0.39	6	0.16	0.07–0.27
1971 Ad	2	0.16	0.10–0.22			
1972 Im	11	0.16	0.09–0.36			
1972 Ad	8	0.24	0.08–0.86			
Ring-necked duck						
Spring 1971	1	0.03				
1972	3	0.08	0.07			
Fall 1971 Im				3	0.08	0.06–0.10
Common goldeneye						
Spring 1971	2	0.63	0.58–0.67			
Fall 1971 Im				1	0.72	
1971 Ad				2	0.12	0.12–0.13
Bufflehead						
Spring 1971	5	0.36	0.10–0.79	4	0.52	0.36–0.84
Fall 1971 Ad				3	0.28	0.10–0.56
Ruddy duck						
Fall 1971 Im	1	0.08				
Hooded merganser						
Fall 1972 Ad	1	0.26				

Mercury levels in fall adult migrants differed from levels in spring migrants in the comparison of 1971 fall dabblers to 1972 spring migrant dabblers returning to the Saskatchewan River Delta. The 1972 spring dabblers averaged 0.18 ppm mercury compared to 0.13 ppm for 1971 fall dabbler adults ($P < 0.001$). This difference may reflect the uptake of mercury on the wintering grounds, the influence of dabblers originating from other areas, or a minor difference in the composition of dabbler species in 1971 and 1972.

The mercury in breast muscle of adult ducks collected in fall 1971 from Lake Winnipeg sites averaged 0.23 ppm for 2 dabblers and 0.16 ppm for 7 divers.

Mallard, pintail, lesser scaup (*Aythya affinis*) and canvasback (*A. valisineris*) (*33*) collected from western Canada in late summer or fall 1969 and 1970, when mercury was used extensively in agriculture as a seed dressing for grain and in fungicides (*5*), revealed lower levels of mercury than the values reported here (Table 1). The present values for breast muscle are comparable to those of Pearce et al. (*21*) for waterfowl collected in eastern Canada during 1971 and 1972. They reported an average of 0.15 ppm in 146 dabbling ducks and 0.13 ppm mercury in 61 diving ducks. These differences may result from the accumulation and magnification of mercury in large, stream-fed habitats compared to a lower potential for mercury concentration in small prairie potholes, and subsequent differing availability to waterfowl.

Immature dabbling ducks from the Delta collections averaged 0.13 ppm ($n = 50$) for 1971 and 1972 while Lake Winnipeg immatures averaged 0.19 ppm ($n = 20$). The immature dabblers from both the Saskatchewan River Delta and the Lake Winnipeg area in 1971 had relatively lower mercury concentrations in their breast muscles than the adults collected during the spring from these areas, although this difference was not significant. There were significant differences between the Delta immatures for 1971 and 1972 (0.15 ppm, $n = 24$, $P < 0.05$). These differences were attributed to the higher mercury load in the breast muscle of immature blue-winged teal (*Anas discors*) in the 1971 Lake Winnipeg sample and in the mallard from the 1972 Saskatchewan River collection. The 1972 immature mallards (0.19 ppm, $n = 10$) had mercury levels that were 58 percent higher than levels in the 1971 immatures (0.12 ppm, $n = 12$). The increase in mercury load in the waterfowl suggests an increase in mercury contamination within the Saskatchewan River Delta, but authors were not able to determine the contamination source.

Immature lesser scaup, common goldeneye (*Bucephala clangula*), bufflehead (*B. albeola*), ring-necked duck (*Aythya collaris*), ruddy duck (*Oxyura jamaicensis*), and canvasback had low levels of mercury in breast muscles; these levels were most similar to those in the immature dabblers. In 1971, immature Lake Winnipeg divers averaged 0.02 ppm ($n = 11$) whereas those from the Delta averaged 0.13 ppm ($n = 14$) in 1971 and 0.15 ppm ($n = 13$) in 1972. There were no significant differences between either years or areas.

Mercury residues in the breast muscle of dabblers exceeded 0.05 ppm in 10 of 239 samples, eight of which were adults. This sample included adult and immature blue-winged teal 1971 fall collections from the Delta and Lake areas, and American wigeon (*Anas americana*) and shoveler collected during fall 1972 from the Saskatchewan River Delta.

These dabblers, shovelers, and blue-winged teal as well as the American green-winged teal (*Anas crecca*) had higher mercury residue concentrations in breast muscle than did other species. The three species do not field-feed so are not directly exposed to treated gain. Thus their mercury uptake must involve aquatic food chains. Feeding studies indicate that these species depend heavily on gastropods and crustaceans (*3, 4, 29, 31*) which are known magnifiers of methyl mercury (*14*). Immatures of these species, which are primarily animal feeders, would be useful indicators of mercury contamination sites. Unfortunately the immature blue-winged teal collected during November 1971 in the Lake Winnipeg area were fledged and therefore may not represent the area of collection.

In 10 of 17 divers, mercury concentration in breast muscle exceeded 0.5 ppm. Goldeneye and bufflehead were collected from both localities during fall 1971. Contaminated lesser scaup were obtained from the Lake area in spring 1971 and from the Delta in fall 1972. Nine of the 10 diver specimens were adult. The percent contamination in divers exceeding 0.5 ppm mercury in breast muscle was higher in goldeneye and buffleheads, 60 percent (3/5) and 33 percent (4/12), respectively, compared to 4 percent (3/69) for lesser scaup.

MERCURY RESIDUES IN LIVER AND FEATHER

Mercury residues in the livers of adult dabbling ducks (Table 2) collected during spring 1971 and 1972 from the Saskatchewan River Delta averaged 0.45 ppm ($n = 12$) and 0.46 ppm ($n = 16$), respectively, whereas the Lake Winnipeg sample of spring 1971 averaged 0.61 ppm ($n = 17$). None of the differences in mercury levels in liver for ducks collected by year, area, or season were significant.

In 1971, livers of immature dabblers from the Lake Winnipeg area contained 0.45 ppm ($n = 9$) while

TABLE 2. *Mercury levels in liver tissue and feathers of 16 species of waterfowl collected in Manitoba during 1971 and 1972*

Species/Season/Age	Saskatchewan River Delta						Lake Winnipeg		
	Liver, ppm Hg			Feathers, ppm Hg			Liver, ppm Hg		
	Number	Mean	Range	Number	Mean	Range	Number	Mean	Range
Mallard									
Spring 1971	3	0.32	0.24–0.43				2	0.35	0.10–0.60
1972	5	0.27	0.17–0.42	5	1.58	1.04–2.51			
Fall 1971 Im	3	0.13	0.05–0.19				2	0.19	0.15–0.21
1971 Ad	1	0.10					1	1.03	
1972 Im	5	0.46	0.06–0.98	5	1.20	0.74–1.83			
Pintail									
Spring 1971							2	0.23	0.20–0.26
Fall 1971 Im	1	0.25					2	0.43	0.21–0.64
1971 Ad	1	0.25							
Gadwall									
Spring 1971	2	0.14	0.13–0.14				1	0.18	
Fall 1971 Im	3	0.17	0.11–0.26						
1971 Ad	1	0.20							
1972 Ad	1	0.40		1	0.80				
American wigeon									
Spring 1971	3	0.13	0.09–0.16						
1972	1	0.04		1	3.06				
Fall 1971 Im	1	0.13					2	0.09	0.05–0.13
1971 Ad	1	0.13					1	0.09	
1972 Ad	1	0.71		1	1.25				
American green-winged teal									
Spring 1971							3	0.34	0.28–0.37
1972	4	0.39	0.31–0.47	4	0.92	0.56–1.37			
Fall 1971 Im							2	0.80	0.66–0.93
1971 Ad	1	0.74							
1972 Im	2	0.31	0.48–1.13	2	2.00	0.79–4.21			
1972 Ad	1	0.66		1	7.02				
Blue-winged teal									
Spring 1971	2	0.84	0.73–0.94				6	0.75	0.25–1.20
1972	5	0.63	0.34–0.94	5	3.16	1.40–6.09			
Fall 1971 Im	1	0.45					1	1.09	
1971 Ad	2	0.43	0.19–0.67				1	1.05	
1972 Im	4	0.16	0.11–0.21	4	1.10	0.39–2.01			
Shoveler									
Spring 1971	2	1.23	0.59–1.86				3	1.18	0.95–1.30
1972	1	1.27		1	10.46				
Fall 1971 Im	1	0.38							
1971 Ad	1	0.39					1	1.02	
1972 Im	1	0.12		1	0.72				
1972 Ad	1	0.97		1	3.44				
Redhead									
Fall 1971 Im	1	0.39							
1971 Ad							1	0.11	
Canvasback									
Spring 1971	2	0.38	0.28–0.48						
Fall 1971 Im	2	0.10	0.07–0.12						
1971 Ad							1	0.06	
1972 Im	1	0.15		1	0.69				
Greater scaup									
Fall 1971 Im							1	0.36	
Lesser scaup									
Spring 1971	3	0.89	0.44–1.40				3	1.00	0.42–2.10
1972	6	0.47	0.16–0.85	6	1.69	1.00–2.98			
Fall 1971 Im	3	0.41	0.31–0.53				1	0.40	
1971 Ad	1	0.55							
1972 Im	5	0.27	0.18–0.37	5	1.25	0.57–2.66			
Ring-necked duck									
Spring 1972	3	0.12	0.05–0.17	3	1.26	0.56–2.33			
Fall 1971 Ad							1	0.58	
Common goldeneye									
Spring 1971	2	3.60	3.60						
Fall 1971 Ad							1	0.58	
Bufflehead									
Spring 1971	1	3.80					4	1.78	1.40–2.40
Fall 1971 Ad							1	0.36	
Ruddy duck									
Fall 1971 Im	1	0.25		1	0.90				
Hooded merganser									
Fall 1972 Ad	1	0.87		1	0.26				

young from the Delta area carried mercury loads of 0.22 ppm ($n = 9$) in 1971 and 0.29 ppm ($n = 12$) in 1972. Manitoba-reared divers exhibited mercury concentrations similar to most immature dabbler species sampled: Lake Winnipeg samples contained 0.45 ppm ($n = 3$) while the Saskatchewan River Delta immatures contained 0.32 ppm ($n = 6$) in 1971 and 0.25 ppm ($n = 7$) in 1972. There were no significant differences between area or within year comparisons of young. Differences did occur between amounts of mercury carried by adults and young within the study areas; in 1971 adult divers from both localities contained higher mercury loads in liver tissue than did the young. Immature dabblers reared in the Saskatchewan River Delta in 1972 had a lower liver mercury load compared to both the spring ($P < 0.05$) and fall adult dabblers ($P < 0.01$), where species composition was nearly identical.

Mercury levels in livers of dabblers collected at Maynard and Sydney Lakes in northwestern Ontario (*6*) were similar to the present results, whereas ducks collected on the more contaminated Ball and Clay Lakes exceed most of the values recorded for both Manitoba localities (Table 2). Slightly higher values of total mercury were recorded in liver of various aged shovelers (*Anas clypeata*) and pintail collected in North Dakota (*19, 30*) compared to these species collected in Manitoba. Vermeer and Armstrong (*33*) reported lower levels of mercury in livers of ducks shot in the three prairie provinces than those reported for Manitoba in the present study, except in a common merganser (*Mergus merganser*).

Feathers collected during spring 1972 at the Delta averaged 1.55 ppm mercury ($n = 9$) for divers and 2.56 ppm ($n = 16$) for dabbling ducks, whereas adult dabblers shot during fall contained 3.12 ppm ($n = 4$). Both the immature dabbling and diving ducks had lower mercury residue levels in their primary feathers than either spring or fall adults. Immature dabblers averaged 1.34 ppm ($n = 12$) and divers averaged 1.11 ppm mercury ($n = 7$). Approximately the same species composition was represented in spring and fall samples.

RELATIONSHIPS BETWEEN MERCURY RESIDUES IN FEATHERS, LIVER, AND BREAST MUSCLE

If the relationship of mercury residues in feathers, liver, or wing muscle to those in breast muscle was known and was reasonably constant, one might use the best indicator in a large-scale sampling program to guard against a potential health hazard.

Several indices have been used: feather to breast muscle, breast muscle to liver (*9, 33*), wing muscle to breast muscle (*2, 34*), and breast muscle to brain (*9*). Authors considered three relationships: feather to breast muscle, feather to liver, and breast muscle to liver. The divers and dabblers were divided by season (spring and fall) and by age (adult or immature) for the data collected from the Saskatchewan River Delta in 1972. Unfortunately, the small size of the sample did not permit comparisons of tissues at the species level.

Dabbler results indicate that feathers containing mercury are ideal for predicting mercury levels in muscle and liver of immatures and spring adults (Table 3). Small sample size and lack of data limit the extent to which data for divers may be appraised. The feather-to-liver relationship was highly significant in immature divers as was the breast-muscle-to-liver comparison of spring adult divers. Flightless young waterfowl, Class IIIa (*11*), would provide an excellent indicator for mercury pollution in natal areas since feather material as illustrated in Table 3 permits the prediction of mercury in tissue such as liver and muscle. Moderate numbers of flightless young are captured each year during banding operations in Canada and the United States (M. Smith, Fish and Wildlife Service, U.S. Department of the Interior and D. Nieman, Canadian Wildlife Service, personal communication, 1977).

Vermeer and Armstrong (*33*) found significant correlation between feather and breast muscle residues in adult pintails collected during fall but not in immatures of the species. This may be a result of the season and availability of food as well as the spatial distribution relative to sources of contamination and to collection sites.

TABLE 3. *Correlation coefficients between mercury levels (ppm) in various tissue combinations for Saskatchewan River Delta waterfowl collected in 1972*

	Dabblers			Divers		
Tissues	Spring Adults	Fall Adults	Immatures	Spring Adults	Fall Adults	Immatures
Feather to liver	0.588* (16)	0	0.665* (12)	0	N.A.[1]	0.821*** (9)
Feather to muscle	0.450* (15)	0	0.814*** (12)	0	N.A.	0
Muscle to liver	0.678** (16)	0	0.617* (12)	0.957** (9)	N.A.	0

NOTE: Sample size is given in parentheses.
$P <$ *0.05; **0.01; ***0.001.
[1] No data available.

A comparison of liver mercury levels in Manitoba ducks with experimental results obtained by Heinz (*15–17*) suggests that the reproduction of divers and possibly some dabbler species (*19*) may be affected by mercury contamination. Heinz (*16, 17*) observed that the reproductive success of second and third generations of mallard hens fed a diet containing 0.5 ppm mercury was lower than in the controls. The growth of their ducklings was also slower than that of the control ducklings. The average liver mercury levels in spring divers from Manitoba exceed 1.00 ppm. This mercury load, accompanied by other stresses (parasite load, pesticide residues) could create some subtle population changes. This requires further study, especially between physiologists and population biologists.

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Organochlorine Residues in Fish of Lake Texoma, October 1979

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ABSTRACT

Fillets from 99 fish, representing 11 species and three areas within Lake Texoma, were examined for residues of common organochlorines. Statistical analyses were conducted to determine the relationship of residues in fish fillets to trophic level and to geographical location of the sample.

Most species contained PCBs at levels up to 1100 ng/g and p,p'-DDE as high as 127 ng/g. p,p'-TDE and o,p'-DDT were not found in carnivores, but were present in herbivores and detritivores in amounts up to 36 ng p,p'-TDE/g and 17 ng o,p'-DDT/g. Heptachlor also was not found in carnivores, but was present as high as 37 ng/g in the other two classes. Chlordane ranged to 24 ng/g and was detected in all trophic levels. Dieldrin and p,p'-DDT were present in detritivores and carnivores up to 144 ng dieldrin/g and 410 ng p,p'-DDT/g. Neither substance was found in herbivores. Mirex, endrin, and heptachlor epoxide were present only at low levels. Statistically significant differences (P = 0.05) were found between trophic levels for seven of the eleven organochlorine compounds. No correlation (P = 0.05) was found between fillet concentrations of any parameter and geographical location of the sample.

Introduction

Lake Texoma is a 36,032-hectare (ha) impoundment located at river mile 726 on the Red River. Completed in January 1944 by the U.S. Army Corps of Engineers, the lake occupies portions of both Texas and Oklahoma (Fig. 1). Lake Texoma was constructed for hydropower generation and flood control, and is also used for water supply, navigation flows, sport and commercial fishing, and recreation. At normal pool level, the maximum depth is 34 meters and the mean depth is approximately 9.4 meters. The water has been described as well buffered with carbonates (pH 8.0–8.7), moderately to highly mineralized, and dominated by sodium and calcium salts of sulfates and chlorides (*5*). The lake is thermally stratified during the summer months, and due to the high chloride content of the water, also exhibits haloclines (*3*).

The Lake Texoma watershed covers 102,899 sq. km and is predominantly cropland and pasture. Principal crops grown in the basin are wheat, cotton, and grain sorghum. Except for petroleum production, there is little industry in the Texoma drainage.

This study was conducted to determine concentrations of selected organochlorine compounds, including DDT and metabolites, chlordane, heptachlor, heptachlor epoxide, dieldrin, endrin, mirex, and polychlorinated biphenyls (PCBs), in fillets from fish of Lake Texoma. In addition, we wanted to ascertain if concentrations of these substances varied with trophic level of the fish or geographical location of the sample.

Sampling and Analysis

Ninety-nine fish, representing 11 species, were collected from three areas of Lake Texoma (Fig. 1). Experimental gill nets and modified fyke traps were used on October 2 and 3, 1979, to collect all fish. No attempt was made to select for particular sizes of fish in the sample, although the sampling equipment was not well suited for taking either very large or very small individuals.

Fish species were grouped into three trophic levels as follows:

Herbivores: Gizzard shad (*Dorosoma cepedianum*)
Detritivores: Carp (*Cyprinus carpio*), channel catfish (*Ictalurus punctatus*), smallmouth buffalo (*Ictiobus bubalus*), river carpsucker (*Carpiodes carpio*)
Carnivores: Striped bass (*Morone chrysops*), white crappie (*Pomoxis annularus*), largemouth bass (*Micropterus salmoides*), blue catfish (*Ictalurus furcatus*), flathead catfish (*Pylodictus olivarus*)

Although the feeding habits of some of these species overlap, these groupings provide general trophic levels. These species were chosen not only based on their trophic level, but also because, with the exception of gizzard shad, they are prime contributors to the commercial or sport fishery.

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FIGURE 1. *Sampling sites on Lake Texoma, October 1979*

A fillet was removed from each fish, wrapped in aluminum foil, and transported to the laboratory where each was frozen for later analysis.

Fish fillet samples were analyzed by Texas Instruments Science Services Division under contract with the Corps of Engineers. Laboratory analysis of the fillets followed methods recommended by the Food and Drug Administration (FDA), U.S. Department of Health and Human Services (*2*). Approximately 25 g fish flesh, free of skin, bone, and organs, was weighed to four significant figures and placed in a Waring blender with an equal volume of sodium sulfate and 150 ml petroleum ether. The mixture was blended at high speed for 2 minutes. The solution was decanted through E.D. 515 fluted filter paper into a 500-ml flask. The residue was extracted with two additional 150-ml portions of petroleum ether as described above, and the extracts were filtered and combined in the 500-ml flask. The blender, filter paper, and contacts were washed with a final 10-ml portion of petroleum ether, and the total extract was transferred to a 500-ml Kuderna-Danish concentrator. The volume of the extract was reduced to 10 ml over an 80°C water bath, and the concentrated extract was quantitatively trans-

ferred to a 125-ml separatory funnel for acetonitrile partitioning.

The natural fish oils were removed from the extract by washing the petroleum ether three times with 40-ml aliquots of acetonitrile in a 125-ml separatory funnel. The acetonitrile was collected in a 1000-ml separatory funnel, and 700 ml water and 40 g sodium chloride were added. This mixture was then extracted three times with 100-ml aliquots of petroleum ether. The combined petroleum ether fractions were transferred to a 500-ml Kuderna-Danish concentrator through a column of sodium sulfate and were concentrated to 10 ml over an 80°C water bath.

This 10-ml sample concentrate was loaded on a prewashed, 10 mm × 30 cm column packed with 12 g Florisil (PR grade) and topped with 1 inch of sodium sulfate. The sample was then eluted from the column with 300 ml of 6 percent diethyl ether in petroleum ether. Each sample was reduced to a final volume of 5 ml in a Kuderna-Danish concentrator and stored at 4°C in a glass vial with a Teflon-lined cap.

The samples were originally analyzed for PCBs as Aroclor 1254, using a Perkin-Elmer 910 gas chromatograph equipped with a ^{63}Ni electron-capture detector. Instrument parameters and operating conditions were as follows:

Column:	6-ft glass, 2-mm-ID, packed with a mixture of 1.5 percent SP 2250 and 1.95 percent SP 2401 on 100–120-mesh Supelcoport
Temperatures:	injector 250°C column 200°C detector 250°C
Carrier gas:	nitrogen flowing at 30 ml/minute
Injection volume:	2 µl extract in petroleum ether

Because a number of the samples exhibited significant peaks at retention times corresponding to chlorinated pesticides, the samples were subsequently analyzed for pesticides, using a Tracor 560 gas chromatograph equipped with a ^{63}Ni electron-capture detector. Instrument parameters and operating conditions for the pesticide analyses were as follows:

Column:	10 meter, 0.25-mm-ID glass capillary coated with OV–101
Temperatures:	injector 250°C column 200°C detector 350°C
Carrier gas:	Helium flowing at 2.5 ml/minute
Make-up gas:	Nitrogen flowing at 70 ml/minute
Injection:	2 µl extract in petroleum ether plus 1 µl isooctane.

Recorder was zeroed with the column at 200°C. Column temperature was reduced to 50°C and an injection was made in the splitless mode for 30 seconds. The injection port was then purged and the column temperature was increased ballistically to 200°C.

Each sample was analyzed for *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, *o,p'*-DDT, *o,p'*-TDE, heptachlor, heptachlor epoxide, dieldrin, mirex, chlordane, and endrin. Detection limit for the above organochlorine pesticide residues was 1.0 ng/g, and 10.0 ng/g for Aroclor 1254. To ensure quality results, a reagent/glassware blank was generated and analyzed with each batch of 20 samples. Five percent of the samples analyzed were re-analyzed by a second person and results were within ± 15 percent. In addition, sequential recovery data and spiked recovery data were generated for 5 percent of all samples analyzed. Sequential recovery yielded 99 percent recovery from the initial extractions. Spiked recovery ranged from 95 to 104 percent. Results were not corrected for recovery.

Statistical comparison of organochlorine residues in fish of different trophic levels was conducted using Newman-Keuls multiple range test. Organochlorine residues in the fillets were correlated with geographical location of the sample by analysis of variance.

Results and Discussion

PCBs (as Aroclor 1254) were found in all species except largemouth bass, and were present in all trophic levels. Eighty-eight percent of the herbivores, 37 percent of the carnivores, and 84 percent of the detritivores contained PCBs. Median and maximum concentrations in the fillets are shown in Table 1. No significant difference ($P = 0.05$) was found between levels of PCBs in detritivores and those in herbivores. PCB levels in fillets of both herbivores and detritivores were significantly greater ($P = 0.05$) than those in carnivores. No significant correlation ($P = 0.05$) was found between levels of PCBs in fillets and geographical location of the sample. None of the fish violated either the FDA current PCB standard of 5 µg/kg or the proposed standard of 2 µg/kg (*1*).

CHLORDANE

Chlordane was present in all herbivores and detritivores except channel catfish, but was found in only two carnivorous species, striped bass and flathead catfish. It was present in 57 percent of the herbivores, 47 percent of the detritivores, and 4 percent of the carnivores. The greatest amount found was 24 ng/g in a smallmouth buffalo (Table 1). Levels of chlordane in fillets were significantly different ($P = 0.05$) in both detritivores and herbivores when compared to carnivores. There was no significant difference ($P = 0.05$) between levels in detritivores and herbivores. No significant correlation ($P = 0.05$) was indicated between chlordane levels in fillets and sample location. Zitko (*8*) deemed similar levels of chlordane in some marine species not toxicologically significant.

TABLE 1. *Concentrations (ng/g) of selected organochlorine residues in fillets of fish from Lake Texoma, October 1979*

Species	Number	PCBs		Chlordane		Dieldrin		Mirex		Endrin		*p,p'*-DDE		*p,p'*-TDE		*o,p'*-DDT		*p,p'*-DDT		Heptachlor		Heptachlor Epoxide	
		Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.	Med.	Max.
HERBIVORE																							
Gizzard shad	14	105	460	2	17	0	0	0	40	0	0	15	505	0	3	0	11	0	0	0	37	0	0
Total	14	105	460	2	17	0	0	0	40	0	0	14	505	0	3	0	11	0	0	0	37	0	0
CARNIVORES																							
Striped bass	8	50	100	0	8	0	0	0	0	0	0	4	37	0	0	0	0	0	410	0	0	0	0
White bass	14	75	110	0	0	0	144	0	0	0	0	4	12	0	0	0	0	0	0	0	0	0	34
White crappie	19	0	100	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0
Largemouth bass	3	0	0	0	0	0	0	0	0	0	0	1	3	0	0	0	0	0	0	0	0	0	0
Blue catfish	2	50	100	0	0	0	0	0	0	0	0	12	20	0	0	0	0	0	0	0	0	0	0
Flathead catfish	1	120	120	5	5	0	0	0	0	0	0	34	34	0	0	0	0	0	0	0	0	0	0
Total	47	0	120	0	8	0	144	0	0	0	0	1	37	0	0	0	0	0	410	0	0	0	34
DETRITIVORES																							
Smallmouth buffalo	13	185	1100	5	24	0	0	0	0	0	13	29	121	0	36	0	14	0	26	0	5	0	0
River carpsucker	11	100	300	1	14	0	0	0	0	0	10	35	127	0	9	0	11	0	10	0	0	0	0
Carp	7	50	100	0	6	0	0	0	0	0	0	8	54	0	0	0	0	0	0	0	0	0	0
Channel catfish	7	50	160	0	0	0	107	0	0	0	0	10	104	0	11	0	0	0	189	0	0	0	11
Total	38	100	1100	0	24	0	107	0	0	0	13	18	127	0	36	0	14	0	189	0	0	0	11

p,p'-DDE

Members of all species and all trophic levels contained *p,p'*-DDE. Levels of this isomer in fillets were as high as 505 ng/g in a gizzard shad (Table 1). By trophic level, 93 percent of the herbivores, 84 percent of the detritivores, and 53 percent of the carnivores contained detectable amounts of *p,p'*-DDE. Levels in fillets were significantly different ($P = 0.05$) between all three groups. No significant correlation ($P = 0.05$) was noted between levels of fillets and the location of the sample.

p,p'-TDE

p,p'-TDE was found in fillets from all species of herbivores and detritivores except carp. Only one shad contained this isomer, but it was found in numerous detritivores at levels up to 36 ng/g (Table 1). It was not found in any carnivores. Detritivores contained significantly higher ($P = 0.05$) levels of *p,p'*-TDE than did either herbivores or carnivores. There was no significant difference ($P = 0.05$) between concentrations of *p,p'*-TDE in fillets of herbivores and those in carnivores. There was also no significant correlation ($P = 0.05$) between levels of *p,p'*-TDE in fillets and geographical location of the sample.

o,p'-DDT

Channel catfish and carp were the only species of detritivores which did not contain *o,p'*-DDT. However, it was found in only one individual herbivore and in no carnivores. The maximum amount found was 14 ng/g in a smallmouth buffalo (Table 1). Significantly different ($P = 0.05$) amounts of this substance were found between all three trophic levels. No significant correlation ($P = 0.05$) was found between levels of *o,p'*-DDT in fillets and sample location. Levels of *o,p'*-DDT found in the present study were similar to levels found by Klassen and Kadoum (*4*) in whole fish samples from a Kansas reservoir. Those authors also found that concentrations were higher in the low trophic levels.

p,p'-DDT

p,p'-DDT was found in all detritivores except carp. It was not found in any herbivores and was present in only one species of carnivore, striped bass. Eleven percent of the detritivores and 4 percent of the carnivores contained *p,p'*-DDT. The largest amount was found in a striped bass fillet, which contained 410 ng/g (Table 1). This high level of DDT suggests recent contamination of this striped bass (*6*). Statistically, there was no significant difference ($P = 0.05$) between *p,p'*-DDT levels in fillets and trophic status. There was also no significant correlation ($P = 0.05$) between *p,p'*-DDT levels and geographical location of the sample.

HEPTACHLOR

Amounts of heptachlor in fillets ranged up to 37 ng/g found in a shad (Table 1). In addition to shad, only smallmouth buffalo contained heptachlor in their fillets. Heptachlor levels in herbivores were significantly greater ($P = 0.05$) than those in either carnivores or detritivores. Levels in carnivores did not differ significantly ($P = 0.05$) from those in detritivores. There was no significant correlation ($P = 0.05$) between levels of heptachlor in fillets and sample location. In a study of 20 Indiana impoundments, Vanderford and Hamelink also observed only small amounts of heptachlor in fish (*7*). In that study, whole fish samples of largemouth bass, sunfish (*Lepomis* sp.), and bullhead (*Ictalurus* sp.) at most contained only trace amounts of heptachlor.

HEPTACHLOR EPOXIDE

Heptachlor epoxide was present in fillets from one carnivore (white bass) and one detritivore (channel catfish). A fillet from the white bass contained the largest amount, 34 ng/g (Table 1). There was no significant correlation ($P = 0.05$) between fillet content and either trophic level or sample location. In the previously mentioned Indiana study (*7*), only trace amounts of heptachlor epoxide were found in the various fish classes.

ENDRIN

Endrin was not detected in any herbivores or carnivores. It was present in only 5 percent of the detritivores and was limited to smallmouth buffalo and river carpsucker. Median and maximum values found in the various species are shown in Table 1. There was no significant correlation ($P = 0.05$) between endrin content of fillets and either trophic class or sample location.

MIREX

No mirex was found in either carnivores or detritivores. Fourteen percent of the herbivores contained mirex at levels up to 40 ng/g (Table 1). Levels in herbivores were significantly greater ($P = 0.05$) than those in either carnivores or detritivores. There was no significant difference ($P = 0.05$) between levels in detritivores and those in carnivores. No significant correlation ($P = 0.05$) was found between levels of mirex in fillets and geographical location of the sample.

DIELDRIN

Dieldrin was found in fillets from only one individual in each of two species. A channel catfish contained 107 ng/g and a white bass contained 144 ng/g (Table 1). Neither value approached the FDA action level of 300 ng/g. There was no significant correlation ($P = 0.05$) between fillet content and either trophic level or sample location.

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Effects of DDE, TDE, and PCBs on Shell Thickness of Western Grebe Eggs, Bear River Migratory Bird Refuge, Utah—1973–74 [1]

Mark L. Lindvall [2] and Jessop B. Low [3]

ABSTRACT

DDE, TDE, and polychlorinated biphenyls (PCBs) as Aroclors 1260 and 1254 were detected in low concentrations in eggs of western grebes (Aechmophorus occidentalis) *from Bear River Migratory Bird Refuge, Utah. DDE was the only contaminant which was both negatively correlated with eggshell thickness and a significant variable in a multiple regression model for predicting eggshell thickness. The eggshell thickness index for western grebe decreased 2.3 percent from pre- to post-DDT-use periods. Incubation stage appeared to have no measurable correlation with eggshell thickness. The small amount of eggshell thinning seen in western grebe eggs at Bear River Migratory Bird Refuge appeared to have no detectable effect on reproduction.*

Introduction

Field studies on shell thinning in fish-eating birds are extensive. Many authors have compared shell thickness or indexes of shell thickness in fish-eating birds between pre- and post-DDT-use periods and found significant decreases (*1, 2, 4, 5, 8, 18*). Studies have also shown a negative correlation between DDE concentration and shell thickness (*1, 2, 5, 8*). Using stepwise linear regression to analyze their data on brown pelican (*Pelecanus occidentalis*) eggs, Blus et al. (*3*) concluded that, of the contaminants measured, DDE had the greatest adverse influence on shell thickness.

Breeding biology of western grebe (*Aechmophorus occidentalis*) was studied at Bear River Migratory Bird Refuge (MBR), Utah, in 1973 and 1974 (*10*). As part of that study, the relationship between pesticide and polychlorinated biphenyl (PCB) contamination and eggshell thickness and thinning was examined. Eggs collected during pre-DDT and DDT-use periods were compared to determine the change in thickness with the advent of DDT use. Multiple regression was used to test the relationship of the various contaminants to eggshell thickness.

Analytical Methods

Ninety-three eggs were collected at Bear River MBF between 1973 and 1974. Eggs were placed in egg cartons and immediately frozen. At the time of analysis, they were allowed to come to room temperature in the laboratory.

Vernier calipers were used to measure length and width (at the widest point) of the eggs to the nearest millimeter. Each egg was then cut at the waist with scissors, and its contents were removed. The inside of the shell was rinsed with water, and the shell was allowed to dry for at least two weeks before any further measurements were made. Six standardized, equally spaced measurements of shell thickness were taken at the waist of each egg, using a Starrett Model 1010 micrometer. Thickness was recorded to the nearest 0.01 mm. Shells were then weighed to the nearest 0.01 g on a torsion balance. Lengths, widths, and weights of eggs from museums were measured by the same techniques as described above. Eggs with a 7-mm or larger blow hole were not measured.

Samples were analyzed at the Denver Wildlife Research Center. Samples were prepared for analysis by the method of Peterson et al. (*14*). Analyses were performed on a Varian Aerograph Model 2740 gas chromatograph. Instrument parameters and operating conditions follow:

Detector:	tritium foil electron-capture
Column:	2-m × 2-mm ID, packed with (1) 3 percent OV-1 on 80–100-mesh Chromosorb W, AW, DMCS; (2) 5 percent QF-1 on 100–200-mesh Chromosorb W, AW, DMCS
Temperatures:	detector 215°C injection port 200°C column 190°C
Carrier gas:	nitrogen flowing at 40 ml/minute

[1] Funding for this project was supplied primarily by the Fish and Wildlife Service, U.S. Department of the Interior, through the Utah Cooperative Wildlife Research Unit. Additional funding was also provided by the Wildlife Society and the Ecology Center, Utah State University.

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Two dissimilar columns were used to confirm the presence of the contaminants. Amounts of DDE and TDE present in samples were calculated by comparing sample peak heights with peak heights of standards. To determine DDE concentration, the sample was diluted until the background PCBs were no longer visible. Amounts of Aroclors 1260 and 1254 were calculated by comparing peak areas of samples with peak areas of standards. Because of peak overlaps, quantities of both TDE and Aroclor 1254 are estimates. That is, area or peak height of underlying PCBs was estimated and then deducted from the observed height or area to obtain the actual peak height due to TDE or the actual peak area due to Aroclor 1254. The lowest quantifiable concentrations were 0.1 ppm DDE and TDE and 1 ppm Aroclors 1254 and 1260.

Results and Discussion

DDE, TDE, and PCBs corresponding to Aroclors 1260 and 1254 were found in various concentrations in western grebe eggs from Bear River MBR (Table 1). DDE was the predominant contaminant detected, averaging 6.6 ppm. TDE averaged 1.3 ppm, and both PCBs, less than 1 ppm; data are recorded on a wet weight basis, and are not corrected for recovery.

TABLE 1. *Organochlorine levels in whole western grebe eggs collected at Bear River Migratory Bird Refuge, 1973–74*[1]

Organochlorine	Basis	Residues, ppm		
		$\bar{x}$	90% CI	Range
DDE	wet	6.6	±1.6	1.0–21.4
	lipid	76.5	±17.7	20–275
TDE	wet	1.3	±0.3	0.3–4.7
	lipid	14.9	±3.1	3–52
Aroclor 1260	wet	<1	—	<1–5.4
Aroclor 1254	wet	<1	—	<1–3.8

[1] $N = 40$.

Ratcliffe (*16*) devised an index to eggshell thickness rather than a directly measured thickness, and that index has gained wide acceptance because it is useful in measuring museum specimens in which a direct thickness measurement cannot be obtained.

Ratcliffe's index is a good estimator of shell thickness in western grebe eggs. The thickness index and average thickness of 93 eggs collected at Bear River Migratory Bird Refuge were highly correlated ($r^2 = 0.7$).

The average eggshell thickness index of the eggs collected at Bear River MBR during 1973 and 1974 was significantly smaller than the same figure for 389 pre-1940 eggs measured in museums ($F = 25.6$, $P < 0.1$). The average thickness index and standard deviation for 93 Bear River MBR eggs was 1.898 ± 0.015 mm and for 389 pre-1940 museum eggs, 1.989 ± 0.008. This is a decrease of 2.3 percent, a small but significant decrease, from pre-1940 to present. Pre-1940 eggs were used in the comparison because they represent a sample obtained before the widespread use of DDT. No difference was seen between pre-1940 eggs collected in California and Utah, and thus the two groups were pooled for the comparison.

The average eggshell thickness (direct measurement) and standard deviation of 93 eggs collected in 1973 and 1974 at Bear River is 0.38 ± 0.03 mm. Rudd and Herman (*18*) give 0.33 mm as the average eggshell thickness of eggs collected at Clear Lake, California, after TDE application to the lake. Eggs at Clear Lake had higher levels of contaminants than those collected during the present study at Bear River MBR. Rudd and Herman (*18*) also took direct measurements from pre-1940 eggs and found an average thickness of 0.389 mm, a thickness 3.1 percent greater than the present Bear River Migratory Bird Refuge collections.

The small amount of eggshell thinning seen in western grebe eggshells at Bear River MBR appeared to have little or no effect on reproduction, because no crushed, cracked, or broken eggs were seen during this study. Average brood sizes of 1.6 in 1973 and 1.8 in 1974 from Bear River compare well with the Rudd and Herman determination of a normally reproducing population (*18*).

Multiple regression with stepwise deletion was used to test the relationship of the various contaminants to eggshell thickness and eggshell thicknes index as was done by Blus et al. (*3*).

The original model for the western grebes, with all contaminants included, explained 45 percent of the variability in eggshell thickness index and 51 percent of the variability in eggshell thickness. In this model the contribution of DDE was significant at the $\alpha = 0.05$ level, and the contribution of Aroclor 1260 was significant at the $\alpha = 0.1$ level. The deletion of Aroclor 1254 and TDE from the model did not lessen the predictive power.

The model containing Aroclor 1260 and DDE explained 50 percent of the variability in eggshell thickness and 45 percent of the variability in thickness index. The contribution of DDE in this model was significant at $\alpha = 0.01$ and the contribution of Aroclor 1260 was significant at $\alpha = 0.025$. This model proved to be the best predictor of both eggshell thickness and thickness index. Deleting Aroclor 1260 from the model and forming a model with only DDE resulted in a loss of predictive power. A model with only DDE explained 37 percent of the variability in eggshell thickness and 33 percent of the variability in thickness index. The contribution of DDE was significant at $\alpha = 0.01$. Table 2 summarizes the various models discussed.

TABLE 2. *Multiple regression models for predicting eggshell thickness and thickness indexes in western grebe eggs, using organochlorine concentrations*

Model	Variable [1]	*F* Ratio	r^2 for Model
$Y_1 = 2.15 + 0.10X_1 + 0.01X_2$	1*	3.1	0.45
$- 16X_3 - 0.04X_4$	2	<0.1	
	3**	5.7	
	4	0.3	
$Y_1 = 2.18 = 0.11X_1 - 0.18X_3$	1**	7.3	0.45
	3***	29.0	
$Y_1 = 2.10 - 0.13X_3$	3***	18.9	0.33
$Y_2 = 42.89 = 1.82X_1 = 0.45X_2$	1*	3.8	0.51
$- 3.12X_3 - 0.83X_4$	2	0.2	
	3***	8.4	
	4	0.5	
$Y_2 = 43.45 = 2.19X_1 - 3.58X_3$	1***	9.4	0.50
	3***	35.6	
$Y_3 = 42.02 - 2.62X_3$	3***	21.4	0.37

NOTE: Y_1 = predicted value of eggshell thickness index; Y_2 = predicted value of eggshell thickness; X_1 = log of Aroclor 1260 concentration, values <1.0 ppm counted as log 0.5; X_2 = log of Aroclor 1254 concentration, values < 1.0 ppm counted as log 0.5; X_3 = log of DDE concentration; X_4 = log of TDE concentration.
[1] Significant at *0.1, **0.05, ***0.01.

The best multiple regression model for predicting both eggshell thickness and eggshell thickness index is the one which includes DDE and Aroclor 1260. Interpretation of this model can be aided by examination of the correlation coefficients (r values) which are given in Table 3. TDE is significantly negatively correlated with both eggshell parameters. Multiple regression analysis suggests, however, that TDE relationship to eggshell thickness and index is spurious, that it is a result of its correlation with DDE. Correlations between both PCBs and eggshell thickness and thickness index were not significant. The contribution of Aroclor 1260 to a multiple regression model was, however, significant. Interpretation of the multiple regression relationship between Aroclor 1260 and eggshell thickness or thickness index is difficult because of this lack of correlation between Aroclor 1260 and either eggshell parameter. One multiple regression model was also tested in which the log of the sum of the PCB isomers was used. This model differed little from the model in which authors considered the PCBs separately. No conclusion on the effect of Aroclor 1260 on eggshell thickness can be drawn from this analysis. The fact that Aroclor 1260 can explain variability in eggshell thickness and thickness index does, however, suggest that there is a possible interaction between Aroclor 1260 and DDE.

DDE was the only contaminant which was both correlated with and could explain variability in eggshell thickness and eggshell thickness index. Experimental studies have shown that DDE in diet can cause decrease in eggshell thickness (*6, 11, 12, 15, 20*). Experimental studies in which birds were subjected to PCBs have not shown reductions in eggshell thickness (*7, 13, 19*). These experimental results support the finding that DDE can be directly correlated to eggshell thinning in the western grebe, but that Aroclors 1260 and 1254 can not. Present analyses do, however, suggest an interaction between Aroclor 1260 and DDE.

TABLE 3. *Correlation coefficients* (r) *comparing organochlorine concentrations and eggshell parameters for western grebe at Bear River Migratory Bird Refuge, 1973–74*

Parameter	DDE	TDE	Aroclor 1254	Aroclor 1260
Thickness	−0.60*	−0.58*	−0.25	−0.01
Thickness index	−0.58*	−0.56*	−0.27	−0.03

NOTE: * Indicates significance at $\alpha = 0.01$.

Incubation stage appears to have no measurable effect on eggshell thickness or index in western grebe. Eggs were divided into four classes according to embryo development, and analysis of variance was used to test for differences between the incubation stages. Groups 1, 2, 3, and 4 contained 50, 19, 8, and 19 eggs, respectively. Significant differences were not detected between groups in either eggshell thickness or index. Declines in eggshell thickness as incubation progressed were reported by Rothstein (*17*) for cedar waxwing (*Bombycella cedrorum*) and by Kreitzer (*9*) for Coturnix quail (*Coturnix coturnix*).

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

AROCLOR 1254	PCB, approximately 54% chlorine
AROCLOR 1260	PCB, approximately 60% chlorine
CHLORDANE	Technical: 60% octachloro-4,7-methanotetrahydroindane and 40% related compounds
DDE	Dichlorodiphenyldichloroethylene (degradation product of DDT)
DDT	Dichloro diphenyl trichloroethane. Principal isomer present (*p,p'*-DDT; not less than 70%): 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane
DIELDRIN	Hexachloroepoxyoctahydro-*endo,exo*-dimethanonaphthalene 85% and related compounds 15%
ENDRIN	Hexachloroepoxyoctahydro-*endo,endo*-dimethanonaphthalene
HCB	Hexachlorobenzene
HEPTACHLOR	Heptachlorotetrahydro-4,7-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-*epoxy*-3a,4,7,7a-tetrahydro-4,7-methanoindan
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
NONACHLOR	1,2,3,4,5,6,7,8,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindan
OXYCHLORDANE	1-*exo*-2-*endo*-4,5,6,7,8,8a-Octachloro-2,3-*exo*-*epoxy*-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene
PCBs (Polychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
TDE	Dichloro diphenyl dichloroethane (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane, principal component)
TOXAPHENE	Technical chlorinated camphene (67–69% chlorine)

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